Background

Among the most exciting tools for the analytical chemist and biochemist are the modern spectrographs which are capable of providing structural as well as compositional information about compounds. While Emission spectroscopy is able to give accurate information as to the type of atoms present in a sample, it cannot give clues to the environment in which each kind of atoms exists. Less energetic methods are required for this purpose so that the integrity of molecules is maintained.

Three principal methods of modern spectrographic analysis are to be examined in this experiment: Mass Spectroscopy, Nuclear Magnetic Resonance, and Infra-Red Spectroscopy. Separately, each gives some information about a substance. Used in concert, they allow the positive identification of many, if not most, <u>organic</u> chemicals. In addition, preliminary classification of many organic compounds is possible through relatively simple qualitative tests similar in scope to those used to identify ions in **The Separation and Analysis of a Mixture**.

Organic compounds are *hydrocarbons*, i.e., they contain at least hydrogen and carbon--often other elements such as nitrogen, oxygen, halogens, phosphorus and sulfur. Most of the bonding involved in organic compounds is covalent. The thermal stability of the compounds is thus less than that of similar molecular mass inorganic compounds. This is one reason less energetic means are used to study their structure.

The physical and chemical properties of organic compounds are highly structure-related. Attachment of small groups of atoms known as *functional groups* to a hydrocarbon can yield a new substance with properties--at least in part--characteristic of that group. Qualitative tests are capable of detecting the presence of such groups. Some common functional groups are listed on the following page for your reference.
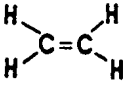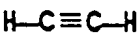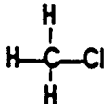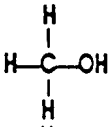
The Qualitative Tests
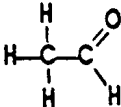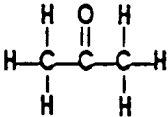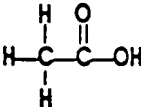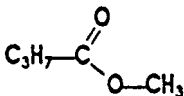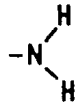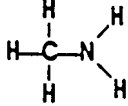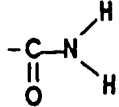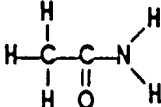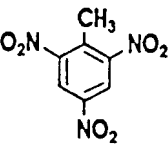
Alcohols are hydrocarbons with -OH replacing one or more hydrogen atoms. Alcohols have physical properties intermediate between those of hydrocarbons and water. Depending on where the -OH group appears, alcohols are classified as *primary* (1°) [on a carbon attached to only one other carbon], *secondary* (2°) [on a carbon attached to two other carbons], or *tertiary* (3°)[on a carbon attached to three other carbons].

Each type of alcohol reacts differently with a strong acid such as hydrochloric acid. The possible product, an alkyl halide, has limited solubility:

$$ROH + HCl \xrightarrow{\text{ZnCl}_2} RCl + H_2O$$
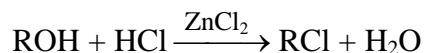
[in this reaction as in most general organic reactions, *R* represents any hydrocarbon group]

This fact is used to advantage in the *Lucas test* in which an alcohol is combined with $ZnCl_2$ and HCl. The formation of the corresponding chloride (analogous to the formation of a chloride salt of a base) results in the separation of the mixture into two layers at varying rates. Tertiary alcohols react almost immediately. Secondary alcohols typically take from 5 to 10 minutes, becoming cloudy before separation occurs. Primary alcohols react very slowly (hours) or not at all.

Sources listed at the end of the experiment.

Functional Group	Name	Type of compound	Example
$C=C$	double bond	alkenes	
$C\equiv C$	triple bond	alkynes	
$-F, Cl, Br, I$	halogen	halides	
$-OH$	hydroxyl	alcohols	
$-C\overset{O}{\underset{H}{}}$	carbonyl	aldehydes	
$-\overset{O}{\underset{}{C}}-$	carbonyl	ketones	
$-C\overset{O}{\underset{OH}{}}$	carboxyl	carboxylic acids	
$-C\overset{O}{\underset{O-}{}}$	-----	esters	
$-N\overset{H}{\underset{H}{}}$	amino	amines	
$-\underset{O}{C}-N\overset{H}{\underset{H}{}}$	amido	amides	
$-NO_2$	nitro	-----	

However, the Lucas test can give many false indications and should not be accepted as foolproof. A study in 1991 by Kjonaas and Riedford pointed out that alcohols which are not sufficiently soluble in the reagent could be mistaken for tertiary or secondary alcohols. They suggested a follow-up test to confirm tertiary alcohols using concentrated HCl only. Tertiary alcohols can be expected to react within 5 minutes whereas secondary and primary alcohols will not react. The test also often fails with secondary alcohols. The authors noted that temperature is important. They suggested 20-25°C. Also, using more alcohol than called for can lead to very long test times. Finally, mixing too much is not better. Swirling vigorously for 3 to 5 seconds and then allowing the mixture to stand appears to give the best results. They added that test times are often longer if the reagent is added to the alcohol rather than the other way around.

Aldehydes and **ketones** can undergo a variety of reactions, but they share many chemical properties with other related compounds such as acids and esters. It is possible to detect uniquely the presence of an aldehyde or ketone by reaction with 2,4-dinitrophenylhydrazine: [shown with the general example of a ketone]
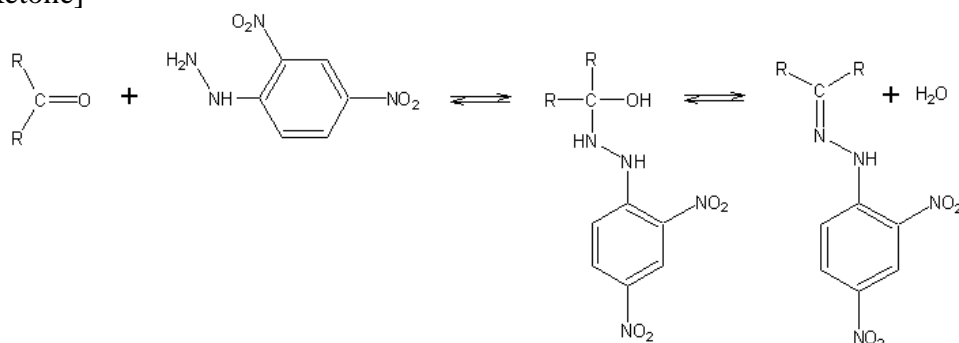
The orange crystalline product is often recovered and used to identify the compound because it has a well-defined (and generally published) melting point. But the formation of the orange crystals is enough to determine that one of these two compound types is present.

Aldehydes can be further screened out by their ease of oxidation. With MnO_4^- aldehydes are oxidized to the corresponding acid and the MnO_4^- is reduced to brown insoluble MnO_2:

$$RCHO + MnO_4^- \rightarrow RCHOH + MnO_2 \quad \text{[not balanced]}$$

The *Baeyer test* for unsaturation also uses permanganate as an oxidizing agent, so some confusion may result if the test with 2,4-dinitrophenylhydrazine is not done first.

Carboxylic acids react readily with sodium hydrogen carbonate, $NaHCO_3$, releasing carbon dioxide gas:

$$RCOOH + HCO_3^- \rightarrow RCOO^- + CO_2 + H_2O$$
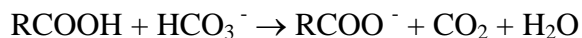
Smaller acids also have a characteristic sour smell, not unlike that of acetic acid (ethanoic acid).

Amines (organic bases) are more difficult to distinguish by chemical tests, but most have a characteristic unpleasant smell which is associated with decomposing animal matter. However since amines and acids are soluble in water to some extent, it is often possible to identify them by the pH of a water solution. Acids will have pH values considerably less than 7 while amines will have values greater than 7. This will generally only work with smaller acids and amines, those having 5 or fewer carbons.

Esters are most often identified by their "fruity" odors but some are rather unpleasant smelling, so this is no sure guide. Esters react with hydroxylamine hydrochloride to yield a compound which can complex with Fe^{3+} to give a colored species:
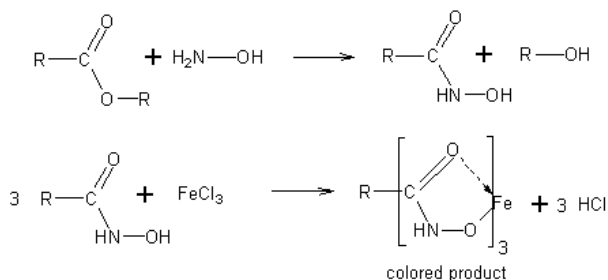
All carboxylic acid esters give magenta colors which vary in intensity depending on structural features in the molecule. Because other types of compounds may also give "positive" tests, a preliminary screening test is generally used to help eliminate false positives.

Compounds which fail to give some kind of positive test indication with the above may fall into the category of simple hydrocarbon (either aliphatic or aromatic), primary alcohol or some other less common type of compound. The only other simple test that can be done on your unknown would be an unsaturation test. To prevent this test from causing misinterpretation of an aldehyde, bromine addition is used instead of the oxidation with potassium permanganate. Compounds with double or triple bonds add bromine readily:
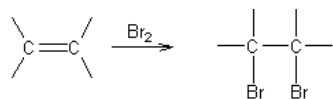
The test is conducted by adding a small amount of the unknown to a solution of bromine in a non-polar and largely inert solvent (generally CCl_4). Addition of bromine and reduction of bond order is accompanied by rapid decolorization.

This completes a background discussion of the qualitative organic tests for those common compounds containing functional groups.

Mass Spectroscopy (MS)

The utility of a mass spectrum for identification arises from the fact that the impact of a beam of electrons upon a given molecule produces a family of ion fragments whose mass distribution is characteristic of the original or *parent* molecule. An accurate measure of molar mass is almost always possible from a mass spectrum, thus making this an invaluable tool in conjunction with purely structural methods such as NMR and IR. In addition, since the fragmentation pattern is reproducible, modern instruments are able to rapidly search databases and compare experimental results with standard spectra for an immediate tentative identification. The kinds of fragments produced also yields information about the strengths of various bonds in the molecule.

In all mass spectrometers a tiny amount of sample is introduced into a high vacuum chamber where it is subjected to an electron stream. These electrons break bonds and form ions from the fragments of the molecule. Electric filtering is used to remove negative ions and the positive ions are then accelerated into the analyzing chamber.

The earliest mass spectrometers relied on a magnetic field to separate the various fragments and send them to the detector:
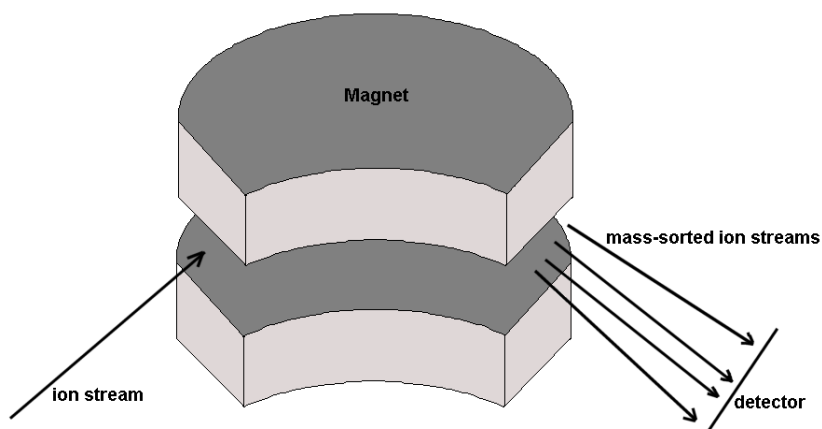
Charged particles passing through a magnetic field travel in curved paths. The curvature of the path is related to the velocity of the particle, its charge and the strength of the magnetic field. In practice only the +1 ions of the fragments produced are used for analysis and so the radius of curvature is based on speed and field strength. Thus ions of different mass could be "swept" across the detector by either changing their speed by adjusting the accelerating voltage or altering the magnetic field strength. Both approaches have been used.

A second approach to the analysis of the fragments is known as "time-of-flight" mass spectrometry. In this type of instrument the ion fragments are given an initial kinetic energy and allowed to "drift" toward the detector. Ions with smaller masses will arrive at the detector earlier than heavier ions:
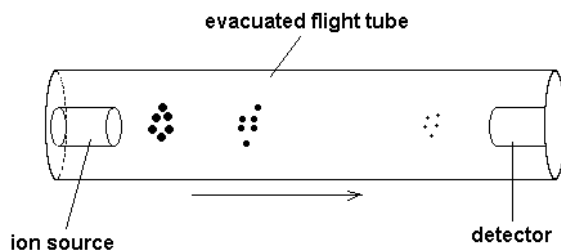
Both types of machines have their advantages but a third design has been used with increasing frequency in modern instrument design owing to its small size and speed. Most often these small spectrometers are coupled with gas chromatographs to provide analysis of fractions as they emerge from the column. The design is known as a *quadrupole mass filter.*

The quadrupole, as the name implies, consists of a set of four electrodes arranged as shown below:
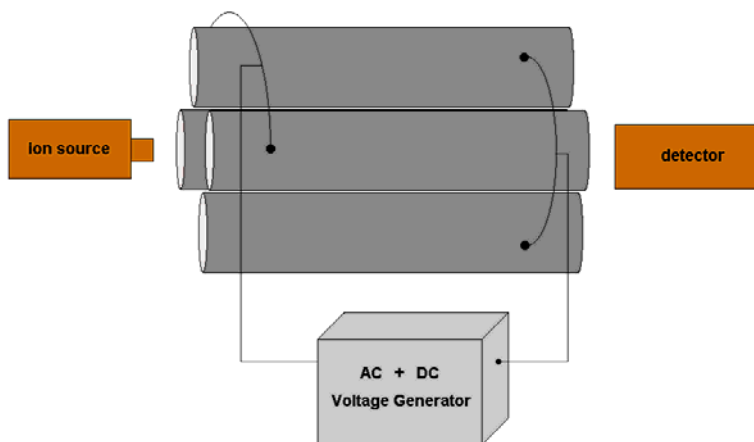
Fragment ions travel from the source, on the left, to the detector on the right, over a relatively small distance and under a moderate high vacuum (10^{-5} mmHg). The "filtering" or discriminating action of the quadrupole is based on two electric currents: one constant (DC), and one which oscillates in polarity with time (AC or RF). The DC current is generally applied to the electrodes at the top and bottom in the diagram and the alternating current is connected to the front and rear electrodes. Control of the oscillation frequency of the AC current and the size of the DC current enables ions of a particular mass (again, all +1) to travel safely through the electrode system and reach the detector. Ions that are either too heavy or too light strike an electrode and are converted into neutral species and eliminated.

A typical mass spectrum such as generated by a modern instrument is shown below:
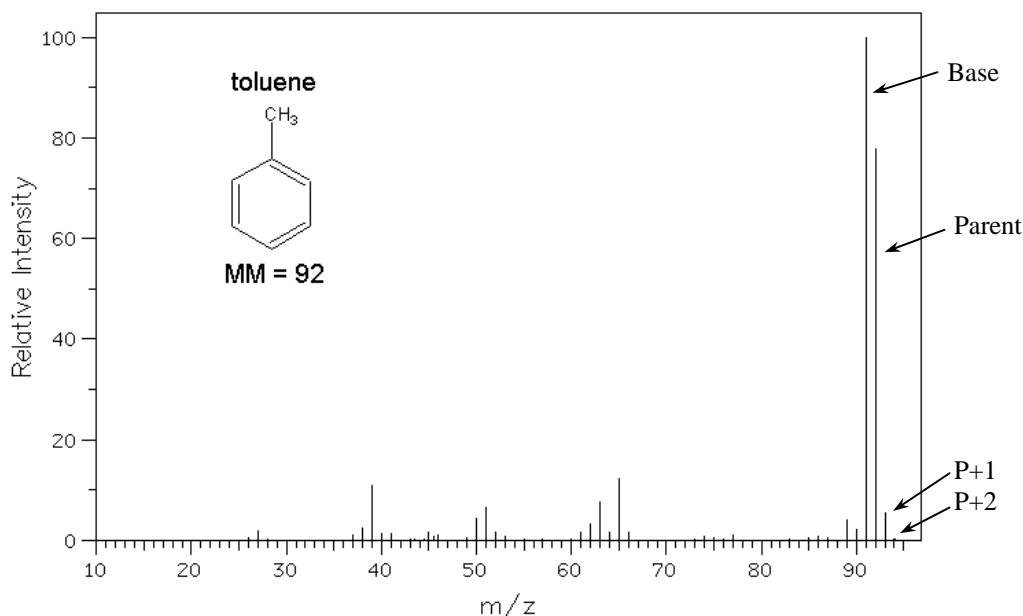
Generally, a **high molar mass peak of varying intensity** is detected as the so-called *parent peak*, indicating the molar mass of the compound. Sometimes this peak is missing owing to the instability of the parent molecular ion in the spectrometer. This can create difficulties in interpretation. The **most intense** peak on the spectrum is known as the *base peak* and the heights of all other peaks are often given as percentages of the base peak height. The intensities of all peaks are proportional to the abundances of the fragments. Smaller peaks scattered throughout the range of masses result from fragments of the original molecule and often provide useful structural information, though positive identification of a substance from mass spectrum data alone is unusual unless a computer-aided search is done. A spectrum such as this would usually be accompanied by a print-out that summarizes the fragment masses and their relative intensities.

Modern mass spectrometers are sensitive enough to detect isotopic differences and elements with reasonably large isotopic compositions can be separated by this method. In this experiment you will use this fact to your advantage. Carbon-13 is present to the extent of about 1% in terrestrial carbon samples. Thus comparison of the height of the peak directly after the parent peak (the so-called P+1 peak) with the height of the parent peak gives information related to the number of carbons in the molecule. This is helpful in generating a possible molecular formula as the examples in a later section will show. A much smaller P+2 peak is sometimes also found, accounting for deuterium and oxygen isotopes. Abnormally large P+2 peaks generally indicate atoms such as sulfur or halogens which have heavier isotopes in relative abundance compared to carbon, hydrogen and oxygen.

Nuclear Magnetic Resonance Spectroscopy (NMR)

Most chemistry students are familiar with the fourth quantum number, m_s, which describes the *spin state* of an electron. Other particles such as neutrons and protons (and even some nuclei) also have two spin states possible: $\pm \frac{1}{2}$. A spinning charge creates a magnetic field and so a proton (in which we are interested here) behaves like a tiny magnet, with the two possible spin states corresponding to different orientations of the magnet:
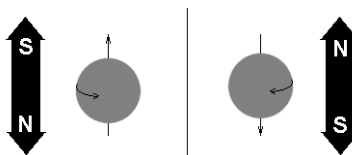
In a typical hydrocarbon sample, the protons (hydrogen nuclei) are randomly oriented with respect to their small magnetic fields. A sample of such a compound, when placed in an NMR spectrometer is subjected to a very strong magnetic field. This causes the proton "magnets" to align in one of two possible directions:

no applied field   applied field
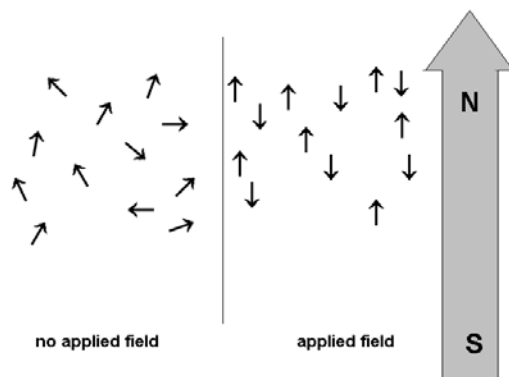
The protons with magnetic fields aligned with the external field have slightly lower energies than those with fields opposed to the external field:
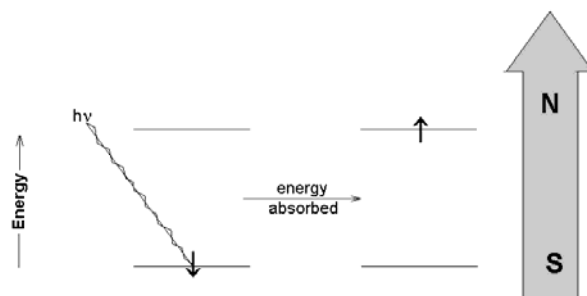
Thus if electromagnetic radiation of the appropriate frequency is used to irradiate the molecule ($\Delta E = h\nu$), absorption of the radiation will occur and protons will move to higher energy states (opposed to the applied magnetic field). The magnitude of the energy split depends on the strength of the applied field, so to make these very small changes as detectable as possible, very large magnetic fields are used.

A simple continuous wave NMR spectrometer (such as the one we have) can be represented by the block diagram below:
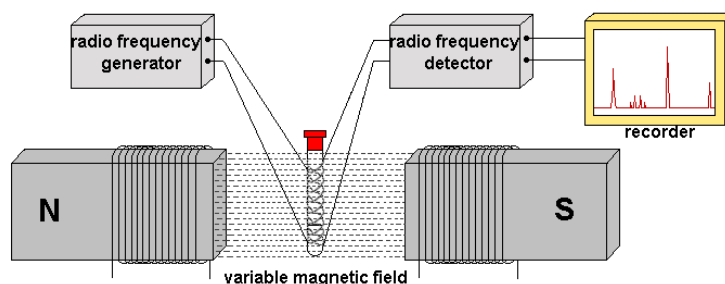
The sample (generally in solution) is placed between the poles of a strong magnet. It is then irradiated with electromagnetic radiation in the radio-frequency range (60.0 MHz for our machine). The radiation absorbed by the sample as the magnetic field strength is varied is measured by the radio-frequency detector (not unlike a very sensitive ordinary radio). The output of the detector eventually ends up at a chart recorder where the spectrum is plotted.

The absorption of the radio-frequency (RF) radiation is called resonance and when this resonance is due to protons in a magnetic field, it is called *proton magnetic resonance*. To distinguish this type of NMR from others it is sometimes called PMR or occasionally ^{1}H-NMR.

The NMR spectrum of a simple compound, CH₃I, methyl iodide, is shown below:
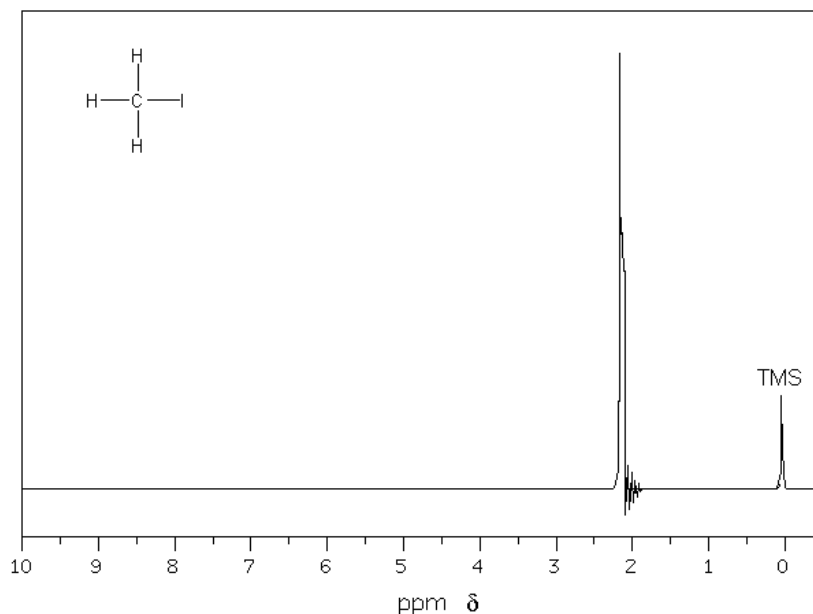
The strong peak or signal at about 2.0 on the bottom scale is from the three protons (hydrogens) in the molecule. The smaller signal at the right is from a reference compound (TMS). More about that later.

As an analytical tool for discerning molecular structure, NMR requires some way of distinguishing protons on one carbon from those on another. This is possible because of the presence of electrons in the molecules. The electrons (which possess the "spin" property) also align with or against the external magnetic field, altering the small magnetic field near the protons. The more electrons that are near a particular proton, the stronger the induced field. This field tends to *shield* the proton from the external magnetic field. Such a proton will require a stronger external magnetic field in order to make a transition (resonance) at 60.0 MHz. This, in turn, will tend to shift the signal farther to the right on the NMR spectrum chart. In fact, the positions of signals on the spectrum are known as "chemical shifts".

Thus in a compound like methyl methanoate (methyl formate), there are two distinct proton environments and therefore two distinct signals on the NMR spectrum:
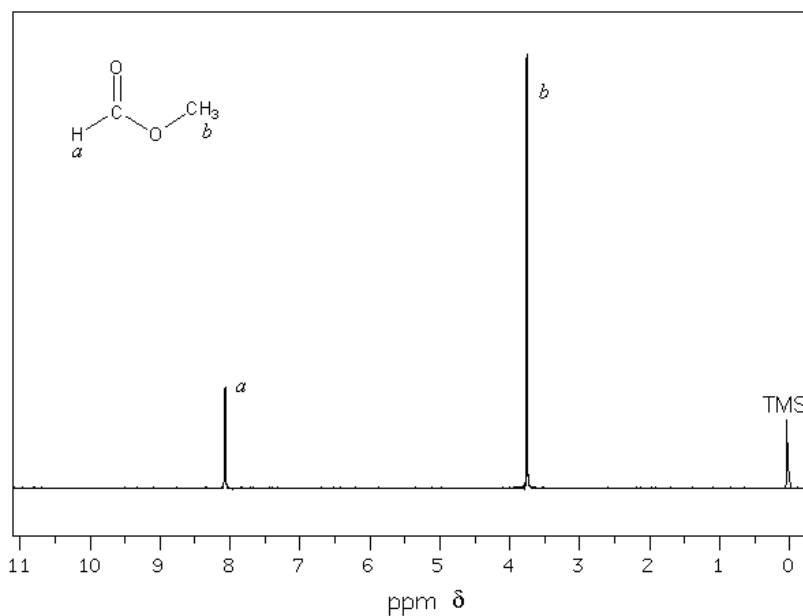
Note that the two signals are also not of the same intensity. The area under each signal peak is proportional to the number of protons that produced it. On an instrument such as the one we will use, a second scan is made after tracing the NMR spectrum. This second scan creates marks on the spectrum chart which help interpret the area under each peak. The tracings are S-shaped and the vertical height of the tracing is proportional to the area under the peak. When the vertical displacements for all the peaks are compared in a ratio, the relative numbers of protons which are responsible for each peak can be determined.

A typical spectrum with the integral trace on it is shown below:
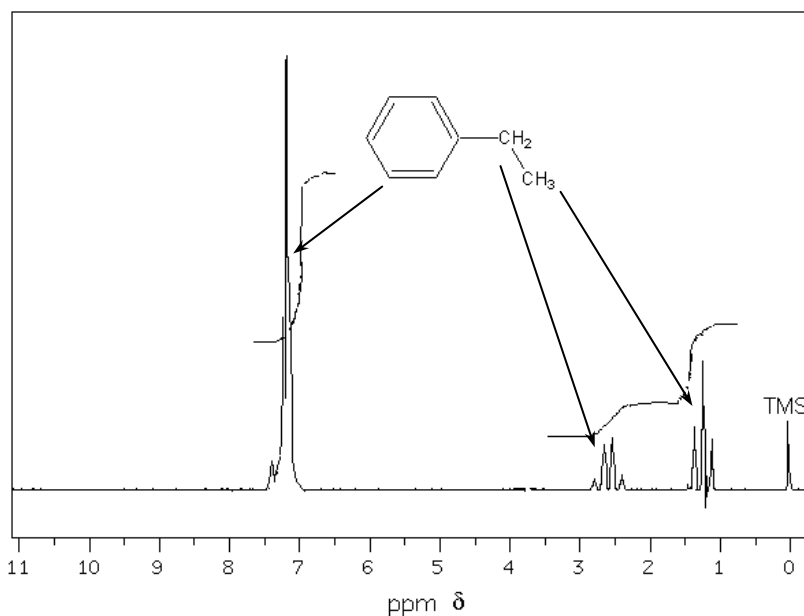
In the molecule ethyl benzene, there are three distinct proton environments, one on the ring (5), one on the carbon directly connected to the ring (2) and one on the terminal carbon (3). If you measure the vertical displacement of each tracing with a good ruler you will see that the ratio of the heights is indeed 5:2:3.

Back to our discussion. Because of the different positions of signals for protons, some standard compound was required for a reference in order to compare signals. Tetramethylsilane, $(CH_3)_4Si$, was chosen for this because it is inert, its twelve protons give a strong signal even when present in only small amounts, and its protons are more strongly shielded than most.

The magnitude of the *chemical shift* of a proton attached to a given type of functional group is relatively constant so that determination of the shifts of various protons in an unknown compound will often provide valuable information concerning the structure of the molecule. Correlation charts are available which give chemical shifts for protons in different molecular environments.

The one remaining major feature of an NMR spectrum which is very helpful in elucidating structure is evident in the spectrum of 1,1,2-trichloroethane (and you may have noticed it above in the spectrum of ethyl benzene).
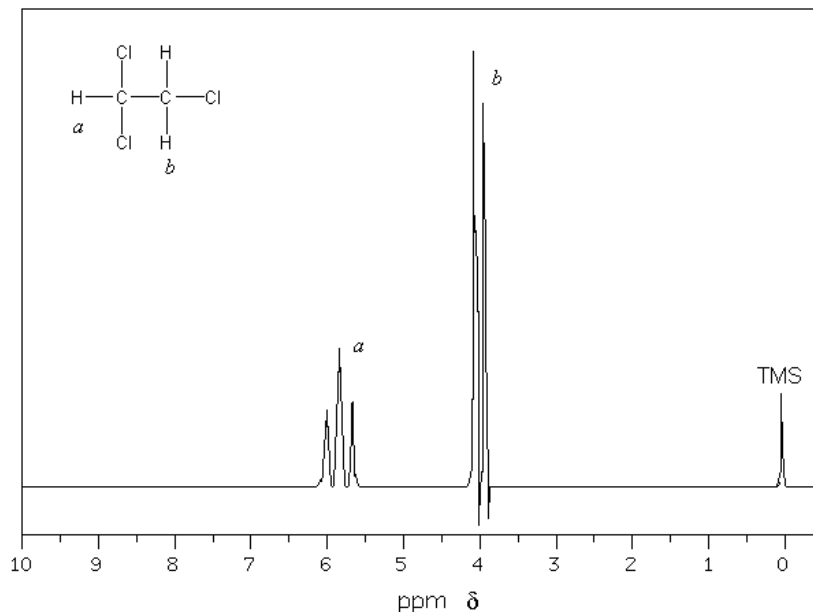
While the areas under the signal peaks are in a 1:2 (*a*:*b*) ratio, the spectrum is more complex than we have seen thus far. We have a *triplet* on the left (*a*) and a *doublet* on the right (*b*). Note that the multiplicity of these signals is <u>not</u> obviously connected with the number of protons that produced them. This kind of splitting pattern for signals is common in NMR spectra and very useful for determining structure. It is called *spin-spin splitting*. Why does this occur?

Protons, behaving like tiny magnets, will exert a small magnetic field on protons on neighboring carbons (the effect is generally too weak to go beyond adjacent carbons). So in addition to the external field and the small fields from electrons, each proton may experience some magnetic field from a neighbor. The effect is to split the signal of the affected proton into $n + 1$ closely spaced peaks, where n is the number of equivalent protons on the <u>adjacent</u> carbon. This is called the "$n + 1$ rule". Applied to the example above, the signal from the (*a*) proton is split into a triplet by the 2 protons (*b*) on the adjacent carbon. And the signal from the (*b*) proton is split into a doublet by the 1 proton (*a*) on the adjacent carbon. The interpretation of this pattern, along with other helpful information, reveals that the protons resulting in these signals are on <u>adjacent</u> carbons.

The pattern of splitting can be explained in this way. Consider proton (*a*). Its signal is affected by the magnetic fields of the two protons (*b*) on the adjacent carbon. These protons could have four possible spin combinations (arrows are used to represent alignment with or against the external magnetic field):
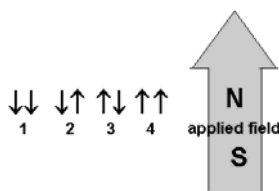
Notice that combinations 2 and 3 are indistinguishable, each with one of the (*b*) protons aligned with the external field and one opposed. We might group these together, then, as shown in the next diagram:

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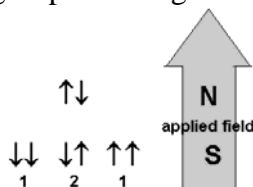
Notice the pattern! The magnetic field created by the middle combination will be twice as strong as that from either of the other two. Thus when these tiny fields interact with the magnetic field of the single proton (*a*), its signal will be split into a triplet with a higher center peak and two smaller side peaks.

You should recognize that this effect only works for non-equivalent protons. For example, the NMR spectrum of ethane, H_3CCH_3, has one and only one signal peak. All six hydrogens are chemically (and magnetically) equivalent.

> The "*n+1*" rule is actually a simplification of a much more complex reality. It is accurate for the example cited previously. Is it less accurate for a molecular fragment such as $-CH_2-CH_2-CH_3$. In that case the methyl proton signal would be split into a triplet and the left-most methylene proton signal would be split into a triplet, but the middle methylene protons should be split into 12 small peaks (the product of the expected effect from each neighbor). Certainly this effect would not be observed on a 60 MHz instrument like ours and it may not be observed to the full extent of 12 little peaks if the magnetic environments of the neighboring protons are very similar. For example, in the structure $H_3C-CH_2-CH_3$ the middle methylene proton signal is split into only a septet because the neighboring effects are truly identical so the "extra" peaks occupy the same place. Practically speaking it is not necessary to know the precise number of little peaks to determine a structure in most simple compounds. The integration ratios provide sufficient corroborative information to establish neighboring proton ratios.

So the combination of chemical shifts and signal splitting patterns makes proton NMR a valuable tool for determining the structure of organic molecules.

Infra-Red Spectroscopy (IR)

Electron beams break molecules into fragments in the mass spectrometer and very strong magnetic fields gently nudge the nuclei of hydrogen atoms into different spin states in NMR. When infra-red radiation interacts with molecules something quite different happens. We are used to thinking of molecules as fixed bodies with definite bond lengths, bond angles and consequent shapes. We know that molecules move from place to place (this is called *translational* motion) using the thermal energy of the environment. Slightly higher energies (in the near infra-red) cause molecules to begin to *rotate*, much as the earth rotates on its axis. As still higher energy infra-red radiation interacts with molecules *vibrational* motion begins. This type of motion can perhaps best be visualized by thinking of a simple diatomic molecule in which the two atoms are small spheres connected by a spring (the bond). In fact calculations of energies involved in molecular vibrations begin as simple spring problems which any elementary physics student would recognize. The frequency (and therefore the energy, $E = h\nu$) of the vibration is related to the strength of the bond (stiffness of the spring) and the masses of the atoms attached, according to Hooke's Law:

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

where k is the "force constant" of the spring or bond, c is the speed of light, and μ is the "reduced mass" of the coupled masses $[m_1 m_2/(m_1+m_2)]$.

In simple molecules the common vibrations can be categorized and some examples are illustrated below:

| symmetrical | asymmetrical | scissoring | rocking | wagging | twisting |
| *stretching* | | | *bending* | | |
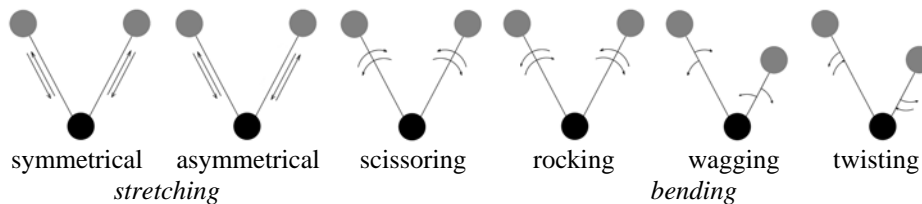
In more complex molecules these and other vibrations may occur simultaneously and interfere with one another as well so the picture becomes very complicated. In addition, although the vibrational energies (frequencies) *are* quantized, discrete absorption spectra are not generally obtained due to the constant rotational motion that accompanies vibration as well as interference between molecules. Band broadening is the typical result.

For routine analysis, the simple stretches are the most helpful in interpreting infra-red spectra. A listing of the major regions would include:

3700 - 2500 cm^{-1}*	X-H stretching (X = C, N, O, S)
2300 - 2000 cm^{-1}	C≡X stretching (X = C or N)
1900 - 1500 cm^{-1}	C=X stretching (X = C, N, O)
1300 - 800 cm^{-1}	C-X stretching (X = C, N, O)

(*infra-red absorptions are generally given in two units: *wavenumbers* and *wavelengths*; wavenumbers, cm^{-1}, are proportional to energy and frequency)

Compared to a mass spectrometer or NMR spectrometer, an infra-red device is relatively simple and is based on a design similar to most optical spectrometers intended for absorption measurements:
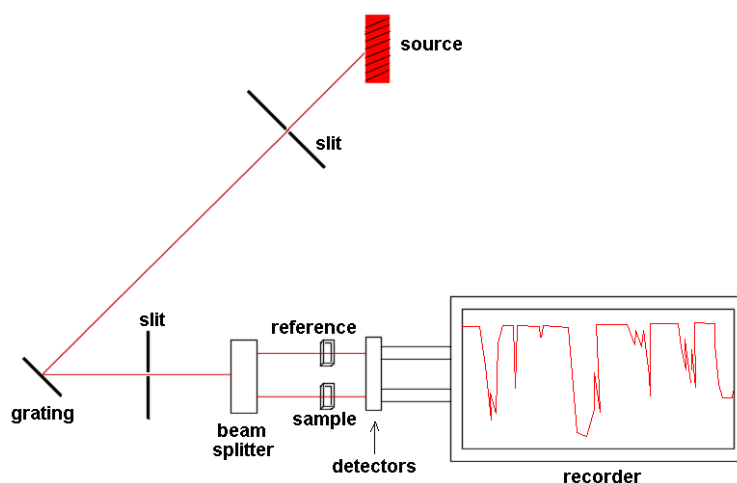
The common infra-red source is an inert solid (metal/ceramic) heated electrically to temperatures between 1500 and 2000 K. Both prisms and gratings are employed for dispersing IR radiation although glass prisms cannot be used since glass absorbs heavily in the infra-red. Quartz and prisms of alkali metal/halide crystals may be used. Various types of thermal detectors are used for the origination of recording signals.

The spectrum of a low-boiling liquid or gas can be obtained after permitting the sample to expand into an evacuated cell. A variety of cells are available for this purpose with pathlengths that range from a few centimetres to several metres (!).

Solutions provide readily reproducible spectra but it is frequently difficult to find solvents that do not themselves absorb in the region of interest. Typical pathlengths are 0.1 to 1 mm. Sodium chloride windows are most frequently employed, although they do become cloudy after a time due to absorption of water. They are thus frequently stored in desiccators.

Pure liquids may be run, but the pathlength must be very small indeed and is frequently achieved by sandwiching a thin film of the pure or "neat" liquid between two rock salt plates giving a pathlength of 0.01 mm or less.

Solids which cannot be dissolved in a suitable solvent can be suspended in a transparent medium called a *mull*. One technique is to grind a milligram or less of the sample with about 100 mg of dried KBr. The mixture is then pressed in a special mill at 10,000 to 15,000 psi to yield a transparent disk. Finely ground samples can also be suspended in oil. Recently a new technique has been used with impressive success. The solid is dissolved in a volatile solvent and the solution is dropped onto a plastic film mounted in a card, similar to a 35 mm slide. The solvent evaporates leaving behind very small crystals suitable for infra-red analysis.

In a usual analysis, then, the sample is placed in the beam of infra-red radiation which is varied in frequency by turning the grating. As the grating moves the detector determines when the intensity of infra-red radiation passing through the sample decreases and sends a signal to a chart recorder which plots out absorbance (or % transmittance) vs. wavelength.

A typical infra-red spectrum is shown below:
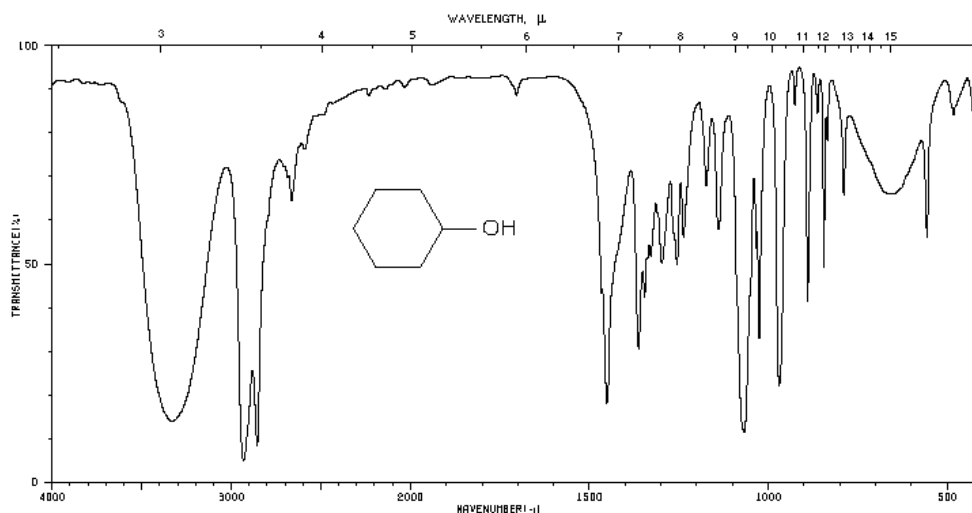
Each "dip" in the line which is traced along the top of the chart indicates a wavelength of infra-red radiation which is absorbed by the molecule because of some vibrational motion. Since similar molecules have aspects of their structures which are similar, they can be recognized by patterns in their IR spectra. At the same time, the uniqueness of the molecular structure of a given compound makes an IR spectrum like a fingerprint for the substance. Correlation charts have been compiled which give group and individual absorbances which result from various structures. For example, the large absorbance at about 3300 cm^{-1} is typical of -OH stretching seen in alcohols like this compound, cyclohexanol.

Of the three types of molecular spectra discussed in the section, IR is probably the most challenging to interpret in detail. Fortunately it is not usually necessary to pin down each and every absorption in order to identify a substance--especially if other data are available.

Interpreting Mass Spectra

A unique molecular formula can usually be derived from a high resolution mass spectrum alone. The table below lists the principal stable isotopes of the common elements and their relative abundances as percentages of the isotope of lowest mass which is set at 100%.

Elements			Abundance %*			
Carbon	^{12}C	100	^{13}C	1.08		
Hydrogen	^{1}H	100	^{2}H	0.016		
Nitrogen	^{14}N	100	^{15}N	0.38		
Oxygen	^{16}O	100	^{17}O	0.04	^{18}O	0.2
Fluorine	^{19}F	100				
Silicon	^{28}Si	100	^{29}Si	5.10	^{30}Si	3.35
Phosphorus	^{31}P	100				
Sulfur	^{32}S	100	^{33}S	0.78	^{34}S	4.40
Chlorine	^{35}Cl	100	^{37}Cl	32.5		
Bromine	^{79}Br	100	^{81}Br	98.0		
Iodine	^{127}I	100				

*Abundance calculated on the basis that the common isotope = 100%

The use of the information in the table may be illustrated by a simple example. Suppose a compound contains one carbon atom. According to the table, about 1.08% of all the molecules will contain a carbon atom with a mass of 13 instead of 12. These molecules will thus have a mass one unit greater than the accepted molar mass of the compound. These molecules will produce a peak at mass P+1 (if the parent peak is taken as mass P) with an intensity or height that is 1.08% the height of the parent peak. And ^{2}H atoms present will also make a very small contribution to the P+1 peak. Large values of P+2 might indicate the presence of, for example, sulfur atoms, or molecules in which several heavier isotopes are present.

Selection of the likely molecular formulas appropriate to a particular parent peak mass and isotope abundance measurements of the P+1 and P+2 peaks is greatly facilitated by the table constructed by Beynon. The table extends from mass 12 to 250 and is limited to compounds composed of C, H, O and N. A program for the TI-83/P calculator which determines the same is available on the Science network (**beynon.83p**).

Example 1

To illustrate the process of interpreting a mass spectrum, consider the example below and the discussion that follows.
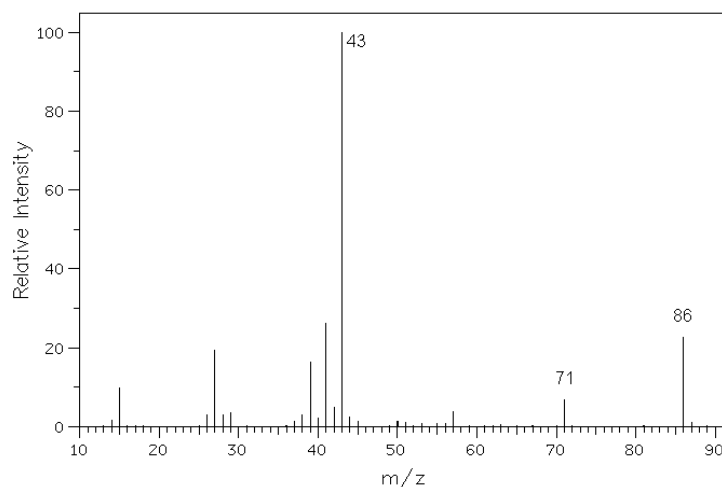
First we locate the **Parent peak**. This is the highest mass peak of any significant size. In this example, the **Parent peak** is at **86**. Thus, the compound has a molar mass of 86 g/mol. Pretty neat, huh? Note that mass 86 is the sum of the integer masses of the *common* isotopes in this molecular formula. Unfortunately the P+1 peak is just barely visible and the P+2 peak is too small to show up on this scan which may have been done at a low voltage. Since this is a common problem with our particular instrument, the instructor will often supply and/or correct the P+1 (and P+2) ratios. For this compound they are 5.5 (P+1) and 0.30 (P+2). These numbers are percentages based on a comparison of the intensities of these peaks compared to the parent peak at 86.

Assuming that this compound is organic, we now need to establish possible formulas which add up to 86. The small size of the P+2 peak suggests that there are no unusual atoms such as sulfurs or halogens. Running the TI-83/P **Beynon** program produces a list of possible formulas. The closest relevant ones are shown below:

	P+1	**P+2**
86		
$C_5H_{10}O$	5.6	0.33
$C_5H_{12}N$	5.98	0.15

From the entries shown it seems that $C_5H_{10}O$ is the most likely formula. It is not always this simple. Isotope ratios are difficult to measure accurately and they should generally be treated as estimates. However, it *is* possible to eliminate the second formula, $C_5H_{12}N$, based on something called the **"nitrogen rule"**. The rule states that **a compound of even molar mass must contain zero or an even number of nitrogens; all compounds with an odd molar mass must contain an odd number of nitrogens**. This rule is based on the bonding properties and outer electron structure of nitrogen. Since the compound in question has an even molar mass, is must contain either zero or some even number of nitrogen atoms.

When elements other than C, H, O and N are present as evidenced by unusually large P+1 or especially P+2 peaks, their kind and number must be determined and their mass subtracted from the parent peak to find the appropriate formula in Beynon's tables. Sizes of the P+1 and P+2 peaks must also be adjusted by subtracting out the contributions of these "hetero" atoms before selecting formulas from the tables. That is not a consideration in this case.

So what else can we say about the mass spectrum at this point? Someone very practiced at interpretation could say a lot more based on the *fragmentation pattern*. It is unlikely that during this experiment you will reach that level of expertise, but that doesn't mean there is no more information. For one thing, the molecular formula suggests a double bond or ring. This is because for 5 carbons the usual number of substituents should be 12 (as in pentane, C_5H_{12}). Since there are only 11 atoms attached to the carbon skeleton in this molecule, there is probably a double bond somewhere. In addition, the peak at 71 suggests (to an old hand) the loss of a methyl group (-CH_3). This is not obvious until you consider that 86 - 71 = 15 which is the mass of -CH_3. The base peak at 43 could be a number of things. There are three listings in the **Table of Common Fragments** at the end of this experiment: C_3H_7, $CH_3C(=O)$, and C_2H_5N. All are plausible with the information we have so far, but the middle one is interesting because it contains a double bond, something for which we are looking.

For now, that's it for the mass spectrum. We can return for a confirmation of the fragments when we know a little bit more about the compound.

Interpreting NMR Spectra

Let's continue with our compound from the previous discussion. The NMR spectrum is given below.
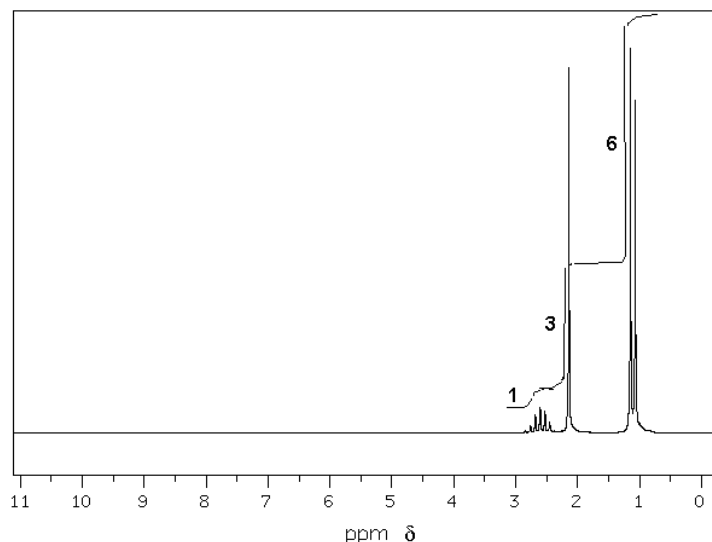
On this spectrum the TMS peak at δ=0 is not shown. Also, the integration ratios are given as integers above each peak. When actually measuring the vertical displacement of the integration tracings you will seldom encounter actual integers, so some adjustment is generally needed. But for this example we can already see that the sum of the integration ratios is 10, which corresponds to only one of the possible formulas: $C_5H_{10}O$ (remember, the signals in an NMR spectrum come from the protons or hydrogens).

The spectrum also indicates that there are three different hydrogen environments in the molecule. One of them, which corresponds to the single peak at about 2.2 is isolated from the other protons and contains three equivalent protons. This would likely be a methyl group, -CH_3. That fits nicely with the fragment we noted as a possibility in the mass spectrum.

The other two proton environments are apparently on adjacent carbons since there is splitting of the signals. The signal at about 1.1 is a doublet. The one at about 2.7 appears at first glance to be a quintet but on closer inspection and with a little thought it is revealed to be a septet. Why?

Remember the *spin-spin splitting* rule. The doublet is produced because the six equivalent protons must be <u>adjacent</u> to a carbon with a single proton (H). For all of this to make sense the signal from the single proton should therefore be split into 6+1 or seven little peaks. No other pattern would match both the integration ratios and the rule. What kind of molecular arrangement would fit this description?

$$\text{CH}_3 - \overset{\displaystyle \text{H}}{\underset{\displaystyle |}{\overset{|}{\text{C}}}} - \text{CH}_3$$
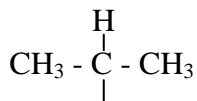
The mass of this fragment, by the way, is 43. That was the *base peak* in the mass spectrum.

Before you start to think this is too easy, you should remember once again that this example is fairly simple and all of the spectra have been selected for their clean form. Reality is something else. Also, the actual chemical shifts of these postulated structures need to be checked in a table to verify these assumptions. The **Table of Common Chemical Shifts** at the end of this experiment indicates the following likely assignments which seem to match the structure we have so far:

$\delta \approx 1.1$ **CH₃** - C -C(=O)R
$\delta \approx 2.2$ **CH₃** -C(=O)R
$\delta \approx 2.7$ **CH** -C(=O)R

The first and last assignments are the protons shown in the fragment above (remember, the first assignment corresponds to <u>6</u> protons). The middle assignment is the isolated methyl group mentioned earlier. If you now count everything up and compare to the molecular formula you will see that we are missing one C and one O. These account for the C=O and lead to a possible structure:
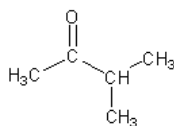
This compound is called 3-methyl-2-butanone and is a *ketone*. It fits all of the information we have accumulated so far. Indeed the structure fits extremely well with the fragmentation pattern of the mass spectrum. A bond scission between carbons 2 and 3 will yield two fragments, both of which have masses of 43. Again, that is the mass of the base peak in the mass spectrum we looked at earlier. The infra-red spectrum is next.

Interpreting Infra-Red spectra

The infra-red spectrum of the compound in question is shown below:
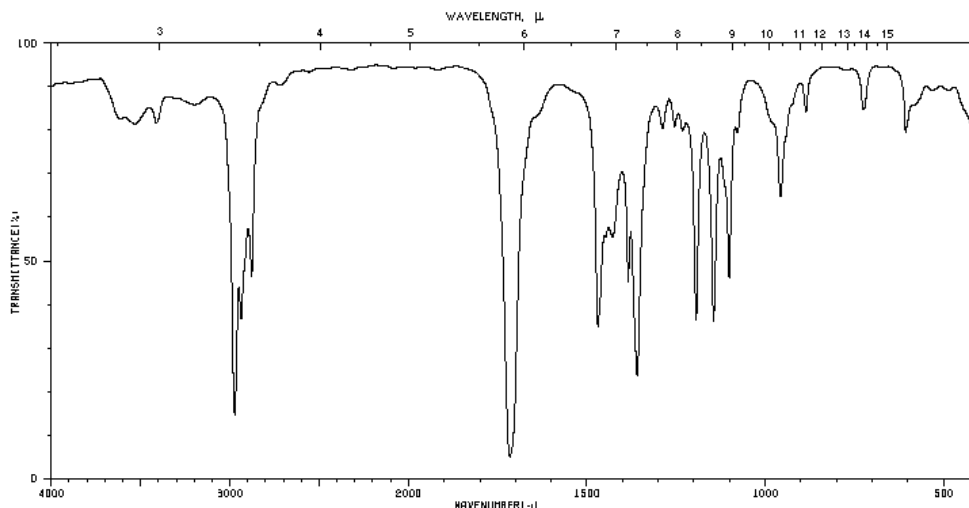
One of the first things to notice about the infra-red spectrum is that there are two scales, one called *wavenumber* and one which is *wavelength*. This is about the only application in which you will see wavenumber which is the reciprocal of wavelength and used because it is directly proportional to the energy needed to excite the vibration. Both scales are used all the time. One advantage to this is that it is often easier to locate a "peak" (really a "valley") with one or the other depending on where it falls on the chart. On this example the wavelength is on the top but sometimes it appears on the bottom. It is also many times a *linear* scale while the wavenumber is not. These spectra have <u>neither</u> scale as linear. The values are the same but the compression factor on either end of the spectrum makes identical spectra from different instruments sometimes look different.

Before going into some detail about this compound it might be a good idea to look at an overview of the region of the spectrum covered by this technique.

———————————————————————————————————

Hydrogen stretching region 3700 to 2700 cm^{-1}

The appearance of strong absorption bands in this region usually results from a stretching vibration between hydrogen and some other atom. The motion is largely that of hydrogen since it is so light; *as a consequence, the absorption is not greatly affected by the rest of the molecule.*

Absorption peaks in the region 3700-3100 cm^{-1} are ordinarily due to various O-H and N-H stretches, with the former tending to appear at higher wavenumbers. The O-H bond peaks are often broader than N-H bond peaks. N-H bond peaks tend to be less intense. Hydrogen bonding will broaden the peaks and move them toward lower wavenumbers. Dilution with a non-polar solvent will sharpen them.

Aliphatic (non-benzene type compounds) C-H vibrations fall in the region between 3000-2850 cm^{-1}. *Most aliphatic compounds have a sufficient number of C-H bonds to make this a prominent peak. Any structural variation that affects C-H bond strength will cause a shift toward or past 3000. Hydrogen on a triple carbon bond occurs at about 3300.* The *hydrogen on the aldehyde functional group usually produces a distinct peak in the region 2745-2700 cm^{-1}.*

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<u>The triple bond region 2700 to 1850 cm^{-1}</u>

A limited number of groups absorb in this spectral region; their presence is thus often readily apparent. Triple bond stretching results in a peak at 2250 to 2225 for a -C≡N: bond, at 2180 to 2120 for a -N≡C: bond, and at 2260 to 2190 for a -C≡C-. Also present are peaks for S-H at 2600 to 2550, P-H at 2440 to 2350 and Si-H at 2260 to 2090 cm^{-1}.

<u>The double bond region 1950 to 1550 cm^{-1}</u>

The -C=O stretching vibration is characterized throughout this region. Ketones, aldehydes, acids, amides and carbonates all have absorptions around 1700. Esters, acid chlorides, and acid anhydrides tend to absorb at slightly higher wavenumbers; that is 1770 to 1725. It is frequently impossible to determine which type of carbonyl (C=O) is present solely from this region. Absorption peaks arising from C=C and C=N stretching are located in the 1690 to 1600 range. Valuable information concerning the structure of alkenes can be obtained from the exact position of such a peak. The region between 1650 and 1450 provides important information about aromatic rings. *Aromatic rings with a low degree of substitution exhibit four peaks near 1600, 1580, 1500 and 1460 cm^{-1}*. Variations on these positions are consistent but independent of substituent, therefore they can give considerable structural information for a substituted benzene ring.

The absorptions in the range 1250 to 500 cm^{-1} cannot usually be associated with vibrational excitations of a particular functional group, but rather are the result of a complex vibrational-rotational excitation of the entire molecule. Accordingly, this part of the spectrum is unique for each substance. It is often called the "fingerprint" region. Two notable exceptions in terms of structural characteristics are important. C-O stretching bands in the region from 1200 to 1100 cm^{-1} are generally strong and broad and would correspond to ethers and parts of esters. Strong peaks in the 840-690 cm^{-1} region are often associated with out-of-plane bending vibrations involving hydrogens on aromatic rings. There are specific patterns which aid in the interpretation of substitution patterns (1,2 or 1,4 as examples).

_____

Returning to the spectrum of the compound, we seem to be faced with a bewildering number of peaks to interpret. Remember, *it is not necessary to interpret every peak*. We are looking instead for evidence in particular regions of the spectrum. Again, expertise comes slowly. The following comments on the spectrum are helpful:

1. there is nothing in the range of 3400-3200 cm^{-1}: no -OH
2. no significant peak at 3100 cm^{-1}: no unsaturated -CH
3. **strong peak at 2900 cm^{-1}: saturated -CH stretch**
4. no significant peak at 2200 cm^{-1}: no -C≡C-
5. **strong peak at 1710 cm^{-1}: carbonyl stretch (-C=O), suggesting aldehyde or ketone**
6. no significant peak at 1650 cm^{-1}: no -C=C-

Notice that not every peak has been addressed. The "fingerprint" region, in particular, has not been mentioned. This would generally be too difficult. However the molecule, which indeed appears to be 3-methyl-2-butanone, has a fairly simple structure and it would be possible to compare its spectrum to the spectrum of other molecules with similar features. Better still, there are vast libraries of spectra (we happen to have such a book) which might even contain this very compound. A visual comparison with a reference would be very satisfying.

Of course, chemistry does not begin and end with spectroscopic analysis. Chemical and physical tests would be entirely appropriate at this point. Checking a simple value like a boiling point or index of refraction would be quick and easy to verify with a handbook.

Example 2

We will now go through a second example to reinforce some of the important points made in the previous problem. Consider this mass spectrum:
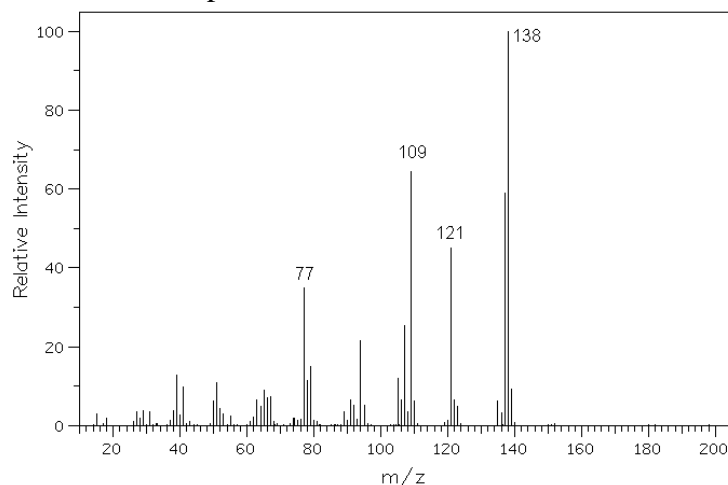
The **parent peak** for this compound (which also happens to be the base peak) appears to be at **138**. The intensities of the isotope peaks are 9.0 (P+1) and 0.65 (P+2). Remember, these are % based on the intensity of the parent peak.

The small size of the P+2 peak suggests that there are no "hetero" atoms. Running the TI-83/P **Beynon** program, the following data is *selected* from the list of formulas:

	P+1	P+2
138		
$C_8H_{10}O_2$	8.88	0.73
$C_7H_{12}N_3$	8.89	0.29
$C_8H_{12}NO$	9.25	0.55

The three entries in the table seem most promising, based on the measured isotope ratios. However, the **nitrogen rule** eliminates the last two because the molar mass of the compound is even and therefore it cannot contain odd numbers of nitrogens. The most likely molecular formula is thus $C_8H_{10}O_2$.

In this case the fragmentation pattern is much more complex than in the previous example. However one feature stands out which is significant to the mass spectroscopist. There is a large peak with a mass one unit less than the parent peak. This "P-1" peak is generally indicative of the easy loss of a hydrogen. Such losses occur frequently with alcohols and aldehydes. The presence of oxygen in the molecular formula is in agreement with either (or both) of these possibilities. In line with this, the peak at 121 could be interpreted as a P-17 peak, indicating loss of -OH. The rest of the spectrum would be difficult to interpret at this point unless you happened to recognize some pattern (unlikely) that you had encountered before. Of course, a good computerized database could pick out a match....

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The NMR spectrum for this same compound is shown below:
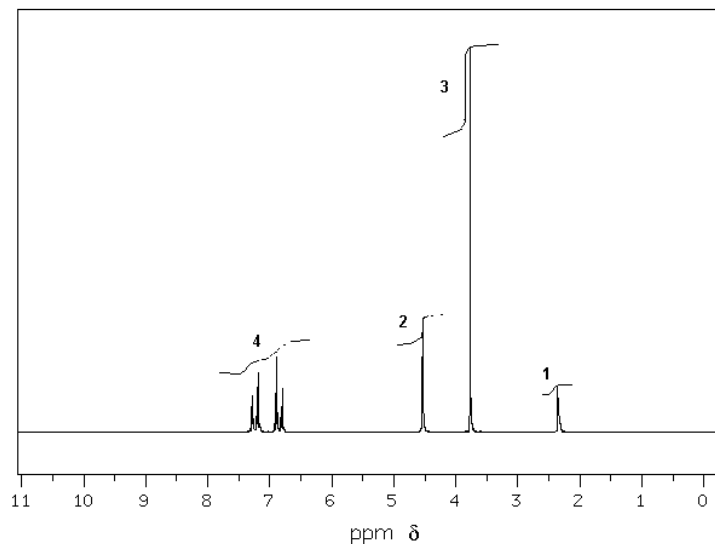
The sum of the integration ratios for the signal peaks is 10. This corresponds to the formula selected as "most likely" earlier, but it also agrees with the two other formulas in the data selected from the **Beynon** program which fit the nitrogen rule, so there is still some room to wiggle.

Based on the signal pattern there are four different proton environments in the molecule. Three of the environments are isolated from the others since the signals are not split into multiplets. The signal centered at about $\delta=6.9$ is a widely spaced quartet. Split signals in this region are most often associated with substituted benzene rings and double bonds. Such a beautifully symmetric split is often an indication of 1,4 disubstitution (or *para* substitution) on a benzene ring. That is something to keep in mind.

You might now begin to recognize that splitting patterns in spectra are actually helpful because we are faced here with three proton environments and only chemical shifts to go on. The singlets at $\delta=3.6$ and $\delta=4.7$ are shifted fairly far to the left and so are probably attached to a rather electronegative group. Remember, increased electron density near a proton tends to shield it from the effects of the external magnetic field and move its signal to the right. So the proximity of an electronegative group which would draw electron density *away* from the protons would tend to shift the signal to the left. In the molecular formula we are working with there are two oxygen atoms--certainly electronegative species. The integration ratios suggest a methyl group ($-CH_3$) and a methylene group ($-CH_2-$).

If we assume that the disubstituted benzene ring is plausible, taken together with the two groups suggested above that accounts for *all* of the carbons in the formula $C_8H_{10}O_2$ and nine of the hydrogens (4 remaining on the benzene ring plus the five from the groups mentioned above). Since there was a strong P-1 peak in the mass spectrum, an alcohol is one possible choice, meaning we would have an -OH group in the molecule and that would account for the last hydrogen and one of the oxygen atoms. That leaves one oxygen atom. Where does it go??????

One important thing to remember about NMR spectra is that *spin-spin splitting* does not occur through oxygen atoms. So the signal from a proton on an oxygen would not be split by the signals from protons on carbons attached to the oxygen.

It is time to look at all the pieces we have one more time:

-CH$_3$ -CH$_2$- -OH   -O-
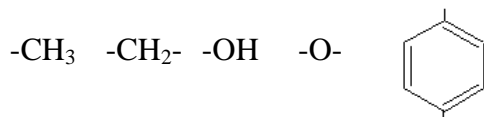
It is tempting to say something about Rocket Scientists here, but for the beginning student trying to make sense out of so much information, structure in molecules is perhaps the *least* obvious part of the story. These are the relevant data from the **Table of Common Chemical Shifts**:

$\delta \approx 6.9$ 1,4-disubstitution on benzene (ethers, alcohols, etc.)
$\delta \approx 4.7$ ϕ-**CH$_2$-OH** [ϕ is used to represent benzene rings]
$\delta \approx 3.6$ ϕ-**O-CH$_3$**
$\delta \approx 2.6$ **-OH** (these span a *wide* range)

A suggested structure would therefore be:
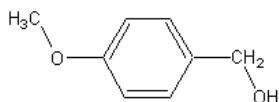
The compound is 4-methoxybenzyl alcohol and is both an ether and an alcohol. In this case the name is perhaps more fearsome than the actual structural analysis. The infra-red spectrum should indicate both of the functional groups proposed as well as the presence of an aromatic ring. It is shown below:
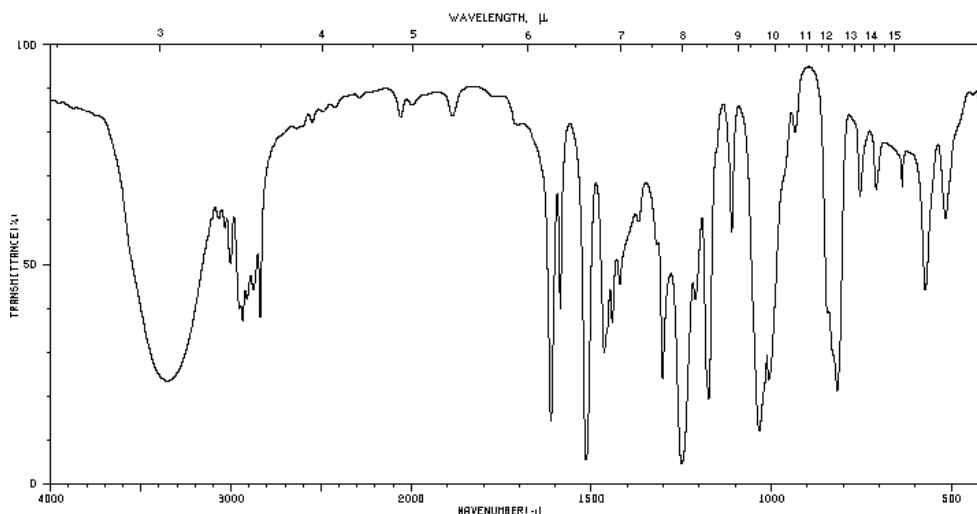
Because the evidence so far strongly suggests the presence of an alcohol, one striking feature of this spectrum is the corroborative evidence of the peak at 3 microns (3200-3400 cm^{-1}). Along with that here are the general comments:

1. **strong peak in the range of 3400-3200 cm^{-1}: -OH**
2. **small peak at 3100 cm^{-1}: possible unsaturated -CH (like in benzene?)**
3. **strong peak at 2900 cm^{-1}: saturated -CH stretch**
4. no significant peak at 2200 cm^{-1}: no -C≡C-
5. no significant peak at 1710 cm^{-1}: no carbonyl stretch
6. **sharp peaks at 1610 and 1500 cm^{-1}: aromatic -C=C-**

In the so-called "finger-print" region there is a lot to look at, but the evidence--as is often the case--is not as clear as the presence of the -OH peak. Absorptions in the 1300-1050 cm^{-1} range could indicate the presence of an ether. The somewhat sharp, medium-sized peak at 1450 cm^{-1} would then indicate that either -CH$_3$ or -CH$_2$- is attached to the ether oxygen on one side. These observations "fit" our compound but are not exactly definitive.

The large, broad peak at about 825 cm^{-1} is in the correct range for 1,4-disubstitution on a benzene ring. But here again it might be helpful to have spectra of similar compounds to compare. Or better yet, a computer database match. The preponderance of evidence, however, indicates that the structure we have chosen is correct. Referring to the **Table of Common Fragments** at the end of the experiment we can even pin down some of the other prominent peaks in the mass spectrum. For example, the large peak at 121 would correspond to CH$_3$-O-ϕ-CH$_2$- (this was also previously interpreted as a possible P-17 peak, indicating the loss of -OH). Physical and chemical tests would be a plus.

Example 3

In one final example before going into the specifics of the experiment we will look at a more systematic approach to the interpretation of the NMR and IR spectra. The mass spectrum for the compound in question is shown below:
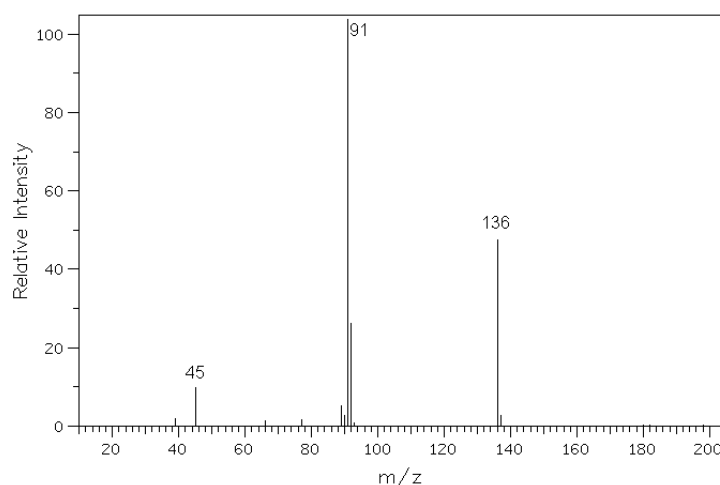
The **parent peak** is clearly visible at **136**. The isotope peaks have intensities of 8.7 (P+1) and 0.6 (P+2). Selected data from the **Beynon** program is given below.

136	P+1	P+2
C$_8$H$_8$O$_2$	8.84	0.73
C$_7$H$_{10}$N$_3$	8.86	0.29
C$_8$H$_{10}$NO	9.22	0.55

Based on the **nitrogen rule** the latter two formulas in the table can be eliminated. C$_8$H$_8$O$_2$ has values for P+1 and P+2 which are closer to the measured intensities. Since there is no prominent P-1 peak, it is unlikely that this compound is either an alcohol or aldehyde. With two oxygens it might possibly be an ester or carboxylic acid, but further information is needed. The base peak at 91 is frequently interpreted as a benzyl unit (ϕ-CH$_2$-) and is a reasonable assumption here considering the unsaturation represented by the molecular formula.

The NMR spectrum for the compound is given below:
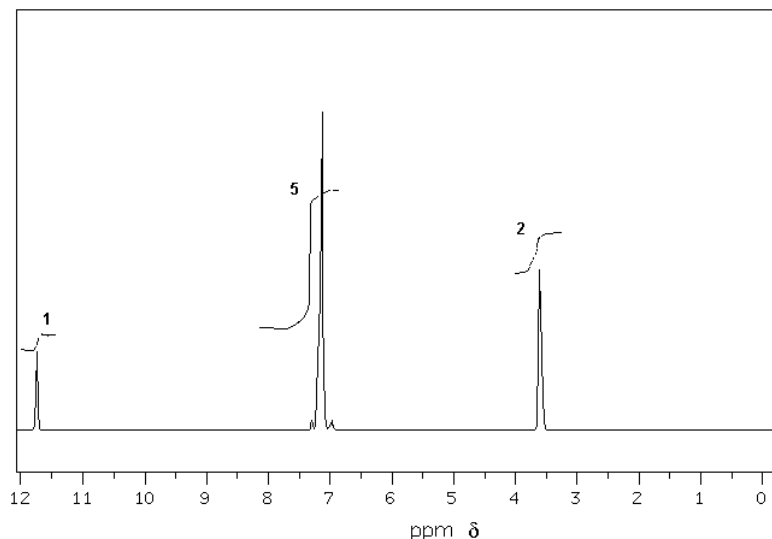
Before looking at a systematic way of analyzing the spectrum, a comment on the signal near δ=7 is appropriate. The beginning student might think this is a triplet. It is not. The most significant reason why it cannot be a triplet is the ratio of peak heights. In a true triplet the height of the central peak should be approximately twice that of the outside peaks (go back to the introductory discussion of *spin-spin splitting* if you do not understand why). Also, the position of the peak indicates that it is probably from a benzene ring and while the "pattern" in the peak may be indicative of the substitution on the ring, it is not a classic splitting pattern from adjacent aliphatic groups. Sometimes small "artifact" peaks are produced by an instrument because of the electronics and the way in which strong signals are processed.

This spectrum shows no obvious splitting patterns, suggesting isolated proton environments. The sum of the integration ratios is 8 which matches our prospective formula. Note that this spectrum also shows an *extended* scale at the bottom. Generally the scale runs from 0 to 10. The signal past 10 would be missed if not specifically sought. Peaks past δ = 10 are often associated with aldehydes and carboxylic acids. However, the lack of a P-1 peak in the mass spectrum suggests that an aldehyde is unlikely.

One way to attack this problem is through a logical sequence of steps that will "fit" just about any basic spectrum. After the sequence has been mapped out we will follow it through for this spectrum and see what we get.

START: compare integration ratios and possible molecular formula; note any splitting patterns

1. **is there a P-1 peak in mass spectrum?**
    --YES: does compound contain N?
        --YES: possible -OH, -C(=O)OH, -NH
        --NO: possible -OH, -C(=O)OH, -CH(=O)
    --NO: probably absent -OH, -C(=O)OH, -NH
2. **does compound contain less than 6 carbon atoms?**
    --YES: aliphatic
3. **are there peaks in the region δ = 10.0 - 6.6**
    --YES: peaks in region near 7.0 may be from one benzene ring if integration ratio <6
        single peaks near or just past 10.0 can be from -CH(=O) or -C(=O)OH
    --NO: go to #7

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4. **does compound contain O?**
    --YES: go to #5
    --NO: peak is from aromatic ring and not -OH, -C(=O)OH or -CH(=O); go to #6
5. **is the peak a singlet?**
    --YES: possible -OH, -C(=O)OH, -CH(=O)
    --NO: two symmetrical doublets may indicate 1,4-disubstitution; other patterns difficult; go to
        #7
6. **is the peak a singlet?**
    --YES: possible symmetrically substituted benzene ring
    --NO: two symmetrical doublets may indicate 1,4-disubstitution; other patterns difficult
7. **are there peaks in the region δ = 6.6 - 4.5?**
    --YES: possible -C(=O)OH, -OH, CHX_2, -C=C-, aromatic secondary amine
    --NO: go to #8
8. **is there a singlet in the region δ = 4.5 - 0.0 with intensity 3 or 3n (n=integer)?**
    --YES: probable $-CH_3$ not coupled to -CH
    --NO: go to #9
9. **is there a triplet + quartet in the region δ = 4.5 - 0.0 with ratio 3:2 or n-multiple?**
    --YES: probable $-C_2H_5$ not coupled to -CH
    --NO: go to #10
10. **is there a triplet+multiplet+triplet in the region δ= 4.5 - 0.0 with ratio 3:2:2 or n-multiple?**
    --YES: probable $-CH_2CH_2CH_3$ not coupled to -CH
    --NO: go to #11
11. **is there a doublet + quartet in the region δ = 4.5 - 0.0 with ratio 3:1 or n-multiple?**
    --YES: probable =CHCH_3 group not coupled to -CH
    --NO: refer to chemical shift tables
12. **Check chemical shift tables**

END

Let's now follow these twelve steps as we look through the NMR spectrum. The answers and comments below are keyed to each of the twelve questions.

1. no, so -OH, -C(=O)OH and -CH(=O) are *probably* absent
2. no, so could be aromatic
3. yes: one peak at about δ = 11.7 could mean either -C(=O)OH or -CH(=O), but aldehyde already
    eliminated in #1, therefore *could be -C(=O)OH*
    one peak at about δ = 7.1 is probably from mono-substituted benzene ring (5 protons left)
4. yes
5. yes for both, likely -C(=O)OH
6. yes, possible mono-substituted benzene ring

**AT THIS POINT: add up fragments found and subtract from molecular formula to obtain
                residue: $C_8H_8O_2$ - (C(=O)OH + C_6H_5) = CH_2**
7. no
8. no
9. no
10. no
11. no
12. residual is $-CH_2-$, corresponds to integration ratio

The likely structural members that result from this analysis are:
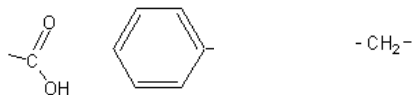
There is only one meaningful way to assemble these in light of what we already know from the mass spectrum (remember the *benzyl* group):
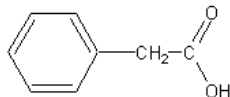
This compound is phenylethanoic acid. The assignments from the **Table of Common Chemical Shifts** are as follows:

$\delta \approx 3.6$ ϕ-**CH$_2$**-C(=O)OH
$\delta \approx 7.1$ monosubstitution on a benzene ring
$\delta \approx 11.8$ -C(=O)O**H**

The infra-red spectrum for the compound is shown below:
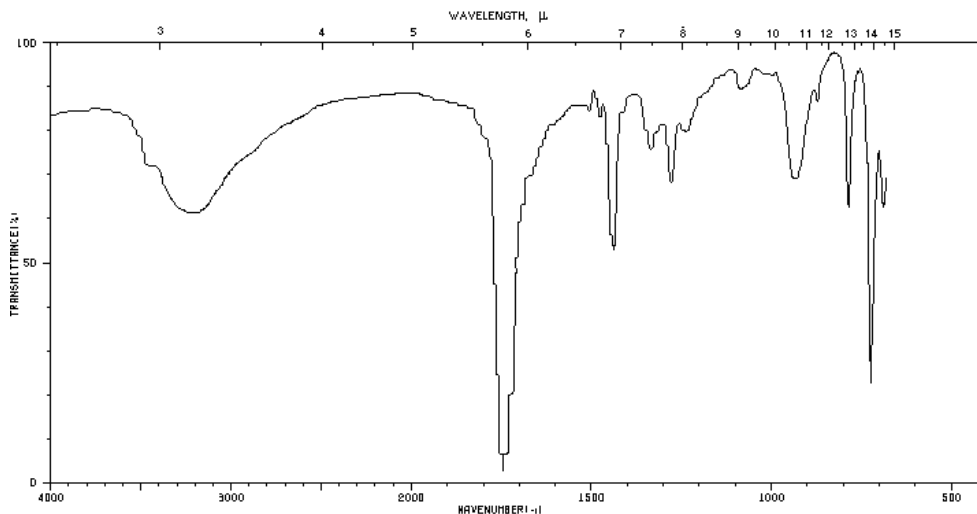
The one really significant feature in this spectrum is the strong and sharp peak at about 1710 cm^{-1} which is indicative of the -C=O stretch (carbonyl). The broadened -CH stretch at about 3100 cm^{-1} may indicate extensive hydrogen bonding. The two peaks at about 700 cm^{-1} and 750 cm^{-1} may be due to the -CH ring plane bending for a monosubstituted benzene ring.

For common types of compounds it is possible to lay out a logical sequence for narrowing down the type of compound based on the infra-red spectrum. Following the same approach as we did earlier for NMR data, a method follows.

START

1. **are there absorptions above 2700 cm^{-1}**
   --YES: very broad and intense?
       --YES: probably -OH
       --NO: go to #2
   --NO: go to #5
2. **is there a weak absorption from 3000-3100 cm^{-1}?**
   --YES: could be aromatic ring hydrogen or alkene hydrogen stretch
   --NO: go to #3
3. **is there a sharp absorption from 2700-3000 cm^{-1}?**
   --YES: could be simple alkane hydrogen stretch
   --NO: go to #4
4. **is there a medium, sharp absorption from 3300-3500 cm^{-1}?**
   --YES: NH (if singlet) or NH$_2$ (if doublet) stretch
   --NO: go to #5
5. **are there absorptions between 2000 and 1500 cm^{-1}?**
   --YES: intense, from 1660-1770 cm^{-1}?
       --YES: probably C=O
       --NO: go to #6
   --NO: C=O, aromatic and secondary amine probably absent; go to #8
6. **is there a sharp, medium absorption close to 1500 or 1600 cm^{-1}?**
   --YES: could be aromatic or secondary amine
   --NO: go to #7
7. **is there a sharp, medium absorption from 1640-1840 cm^{-1}?**
   --YES: probably an alkene
   --NO: go to #8
8. **are there absorptions between 1500-1100 cm^{-1}?**
   --YES: intense between 1050-1300 cm^{-1}?
       --YES: could be C-C, C-O, or C-N stretches
       --NO: go to #11
   --NO: C-O, C-N, CH$_2$, CH$_3$ probably absent; go to #11
9. **is there a medium, sharp absorption at 1375 cm^{-1}?**
   --YES: could be -CH$_3$
   --NO: go to #10
10. **is there a medium, sharp absorption at 1450 cm^{-1}?**
    --YES: could be -CH$_2$- or -CH$_3$
    --NO: go to #11
11. **are there <u>strong</u> absorptions below 900 cm^{-1}?**
    --YES: sharp at 720 cm^{-1} could be -CH$_2$-
    --OTHERS: aromatic*, alkene or monochloro C-Cl possible

END

* aromatic substitution patterns (may not show):   mono 710-690 cm^{-1}
    770-730 cm^{-1}
    1,2-di 770-735 cm^{-1}
    1,3-di 735-680 cm^{-1}
    810-750 cm^{-1}
    1,4-di 860-800 cm^{-1}

O.K., now lets try that with the infra-red spectrum for the compound.

1. no, so not alcohol
2. yes, so could be benzene ring or alkene
3. no, so perhaps not much aliphatic character
4. no, so not an amine
5. yes, so C=O is probably present
6. no
7. no, so probably not alkene (could be obscured by strong C=O peak)
8. no, only weak absorptions so probably not C-O, C-N or others
9. no
10. yes, but maybe shifted a little (nothing's perfect): probably -CH$_2$-
11. not at 720 cm^{-1}, but at 700 and 750 cm^{-1}, match for mono-substituted benzene

The conclusion we reach from this is that we have a mono-substituted benzene ring with a -CH$_2$- and a carbonyl group (C=O) somewhere. The molecular formula and other evidence in concert with this is strongly supportive of the phenylethanoic acid structure. Correlation tables for the IR spectra (at the end of this experiment) indicate that the medium broad absorption centered at about 900 cm^{-1} is from the dimer of the carboxylic acid (carboxylic acids often form *dimers* through hydrogen bonding). Obviously simple chemical tests would help to confirm that this substance is a weak acid.

This completes the introduction to the instrumental portion of the experiment.
_____

The Experiment

There are three parts to this experiment:

- functional group qualitative analysis of the unknown(s)
- molecular spectroscopy of the unknown(s) (MS, NMR, IR)
- two physical tests of the unknown(s)

The following non-locker materials will be provided:

- 10 mL uncalibrated pycnometer
- 6 x 50 mm test tubes and capillary tubes

The Chemicals

2,4-dinitrophenylhydrazine (2,4-DNPH), $C_6H_3(NO_2)_2NHNH_2$, is a red, crystalline powder that is slightly soluble in water and soluble in dilute inorganic acids. It is used for the determination of aldehydes and ketones and for the preparation of their derivatives. The solution used for these tests is tenacious with skin and contact should be avoided. Gloves are ***strongly*** recommended when using 2,4-DNPH. The dry solid is a suspected mutagen.

2,4-dinitrophenylhydrazine
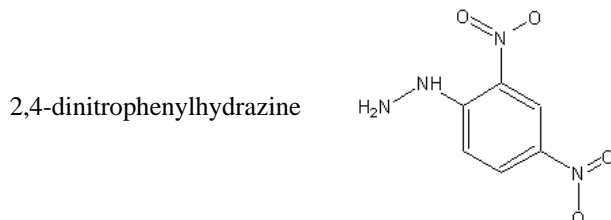
Potassium permanganate consists of dark purple or bronze-like crystals and is a strong oxidizing agent. It is used extensively in laboratory work and also in dyeing wood, bleaching, photography, and tanning. Dilute solutions are mildly irritating to the skin and high concentrations are caustic. Potassium permanganate stains skin and clothing like silver nitrate.

Hydroxylamine hydrochloride (HH), $NH_2OH \cdot HCl$, consists of white crystals which slowly decompose when moist. The solid is fairly soluble in water, less so in ethanol and methanol. It is used as a reducing agent in photography and as an antioxidant for fatty acids and soaps. It may be irritating to the skin, eyes and mucous membranes.

Iron(III) chloride is a very hygroscopic reddish to yellow-brown solid generally found as the hexahydrate. It is readily soluble in water and acetone. The pH of 0.1 M solutions is 2.0. It is used in photoengraving, manufacture of other iron salts, inks, dyes and as a catalyst in organic reactions. Medically it has also been used as a topical astringent and styptic as well as in a test for phenylketonuria.

Sodium hydroxide is commonly known as lye or caustic soda. It is a very hygroscopic white solid (absorbs water from the air rapidly) and also absorbs CO_2. It is very corrosive to vegetable and animal matter and aluminum metal, especially in the presence of moisture. Dissolving NaOH in water generates considerable heat.

Besides its use in the laboratory, sodium hydroxide is used in commercial drain cleaner preparations, to treat cellulose in the manufacture of rayon and cellophane and in the manufacture of some soaps. It is corrosive to all tissues and can be detected on skin by the "slimy" feeling associated with bases. It should be rinsed off thoroughly upon contact. It can damage delicate eye tissues and cause blindness.

Hydrochloric acid is also known as muriatic acid. It is the same liquid acid that is often used in controlling the pH of swimming pool water. It is sometimes colored yellow by iron impurities, traces of chlorine and organic matter. Reagent grade HCl contains about 38% hydrogen chloride gas, close to the limit of its solubility at room temperature.

Hydrochloric acid in concentrated form (12 M) has the sharp, choking odor of hydrogen chloride. It is used in the production of other chlorides and in refining some ores (tin and tantalum), cleaning metal products, removing scale from boilers and heat-exchange equipment, and as an important laboratory reagent (often in diluted form).

Concentrated solutions cause severe burns; permanent visual damage may occur. Inhalation causes coughing, choking; inflammation and ulceration of the respiratory tract may occur. Ingestion can be fatal.

Zinc chloride (used in the Lucas Reagent) is white, odorless, very deliquescent and highly soluble in water. The aqueous solution is acid to litmus (pH 4). It is used as a deodorant, for disinfectiing and enbalming and in the manufacture of parchment papers. It has also been used in a presevative for anatomical specimens. It is moderately irritating to the skin.

Dichloromethane, CH_2Cl_2, is a colorless liquid. The vapor is not flammable. It is soluble in about 50 parts water and miscible with ethanol. Used as a solvent for cellulose acetate and for degreasing, the liquid has been used in the past as an inhalation anesthetic. It is narcotic in high concentrations.

Bromine (used in a solution of dichloromethane) is a dark reddish-brown fuming liquid at room temperature, consisting of diatomic molecules. In dilute water and hexane solutions its color varies from golden to dark orange. In basic solutions at room temperature it slowly reacts to form bromide and hypobromous ions. It is a member of the halogen family and has a chemistry similar to chlorine. It attacks all metals and organic tissues and vaporizes readily at room temperature. Fumes are highly irritating to eyes and lungs.

Bromine is used for bleaching silk, disinfecting spas, and manufacturing anti-knock compounds. Pure liquid bromine on the skin can cause painful, serious burns which heal only slowly.

2-propanone (commonly known as *acetone*) is a volatile, highly flammable liquid with a characteristic odor and sweet taste. It is completely miscible with water, forming a low boiling azeotrope which speeds evaporation and drying (hence its frequent use in rinsing wet glassware and washing precipitates). It will attack many plastics including some synthetic fabrics such as rayon.

2-propanone is used as a solvent for fats, oils, resins, waxes, lacquers, and rubber cements. It is also used in paint and varnish removers (some formulations of fingernail polish remover contain acetone). Prolonged or repeated topical exposure may cause skin dryness. Inhalation may produce headache, fatigue, and in large amounts, narcosis. Serious poisoning is rare.

The unknowns, for obvious reasons, cannot be listed here in detail. They have been chosen for their *relatively* low toxicity and hazard. Some have moderately high vapor pressures and unpleasant odors. All should be treated with caution and skin contact should be avoided. Waste solutions from qualitative tests should be deposited into a container in the fume hood, <u>not</u> flushed down the sink. *Residual material in test tubes or beakers should be removed with a rinse of a <u>small</u> amount of methanol. The rinsings should be added to the waste container.*

Technique Discussion

You will be provided with a small sample (approximately 15 mL) of an unknown organic liquid. You are to determine its identity by instrumental, physical and chemical means. In general, the parts of the experiment may be done in any order, depending on the availability of instruments. The logical approach set out below is only a guideline.

- The organic qualitative tests can be used to narrow down the type of compound.
- The **HP 5890 GC/5970 Mass Spectrometer** can be used to obtain the molar mass and fragmentation pattern.
- The **Beynon** program will make it possible to determine the likely molecular formula of the compound.
- An NMR spectrum, using the **EM-360 NMR Spectrometer,** should be used for structural information.
- An IR spectrum, using the **Perkin-Elmer 1420 IR Spectrometer**, may be used to confirm functional groups and other structural details.
- Physical tests should be done to provide corroborative data. Two of the following are required:
  - boiling point [in some cases this will exceed the range of our thermometers]
  - density
  - index of refraction

The qualitative tests that follow will help you to distinguish among the following types of compounds: ketones, aldehydes, esters, and different alcohols (1°, 2°, 3°). The flow scheme below gives a general outline of the sequence to be used.
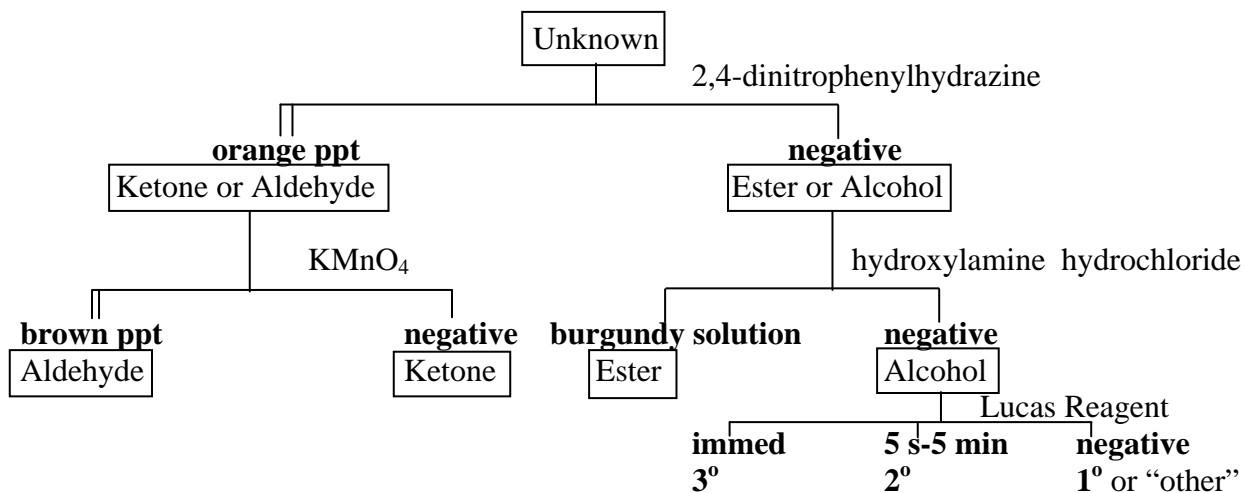
In addition to the series of tests outlined above, you should keep in mind that *hydrocarbons of less than 5 carbons are generally water soluble*. Carboxylic acids vary in solubility but their solutions will generally give a distinctly "acid" reading with pH paper.

Unsaturation (as in alkenes or alkynes) can easily be detected by the <u>immediate</u> decolorization of added bromine. Some bromine dissolved in CH_2Cl_2 will be available for you to use. HANDLE IT WITH CARE. Do this test in the hood.

Several types of compounds are not mentioned at all. These include the simple hydrocarbons (no functional group, either aliphatic or aromatic), ethers, halides, nitriles, nitro-compounds, etc. For the purposes of this experiment you may assume that any compound which tests *negative* for all of the tests given may fall into one of these categories *or may be a primary alcohol*.

Finally, it may be helpful to remember that most common aromatic compounds are benzene-based. Benzene is C_6H_6. Any substitutions on the benzene ring may raise the hydrogen:carbon ratio, but it is still lower than what would be expected in aliphatic compounds. Look for this characteristic in your likely molecular formulas. It can save you a lot of time.

A more detailed description of the qual test scheme follows. **REMEMBER**, these substances should all be considered toxic. The less you use, the less there is to discard. Follow the directions closely as to the amounts of materials. More is not better. Generic "knowns" are available for each test.

(1) 2,4-dinitrophenylhydrazine (2,4-DNPH) test: to about 5 drops of 2,4-DNPH add a drop or two of your unknown. Ketones and aldehydes react immediately, forming unmistakable bright orange precipitates.

(2) $KMnO_4$ test: if the 2,4-DNPH test is positive, add 1 drop of the $KMnO_4$ solution to about 5 drops of your unknown. Aldehydes are readily oxidized to form brown precipitates. Ketones do not react.

(3) Hydroxylamine hydrochloride (HH) test: if the 2,4-DNPH test was negative, mix 1 mL of ethanol and 1-2 drops of the unknown; add 1 mL of 1 M HCl. Note the color produced when 1 drop of 5% $FeCl_3$ is added. If the color is orange, red, blue or violet, the following test will *not* yield valid results and should not be done. Mix 1-2 drops of the unknown, 1 mL of HH and 0.2 mL of 6 M NaOH. Heat to boiling [**CAUTION!!** it boils almost immediately and the mixture is flammable!!], cool slightly and add 2 mL of 1 M HCl. If the mixture is cloudy, add more (about 2 mL) ethanol. Add 1 drop 5% $FeCl_3$ and observe the color. If the color is burgundy or magenta as compared to yellow in the preliminary screening test, an ester is probably present.

(4) Lucas test: if all other tests have proven negative, you may have a simple hydrocarbon, acid, amine or alcohol. Place 10 drops of Lucas reagent in a small test tube. Add one drop of your unknown and swirl vigorously for 3-5 seconds. Allow to stand without further mixing. Tertiary alcohols (3°) react immediately to form a cloudy solution. Secondary alcohols (2°) take from 5 seconds to 5 minutes to form a cloudy solution. Primary alcohols do not react. Be sure to review the background information about the Lucas test given in the introductory remarks. [2-propanol reacts in about 15 minutes using this method]

If all of these tests are negative, you may have an acid or amine which *may* be detected by adding a small amount of the compound to water and testing the mixture with pH paper. Simple unsaturated hydrocarbons are best detected by the Br_2 addition test. However, the presence of other unsaturations (such as carbonyls) can give confusing results. Generally, alkenes react *immediately* while other groups react more slowly. To do this test add 2 drops of your unknown to two drops of the Br_2/CH_2Cl_2 mixture and swirl to mix. Rapid decolorization indicates the presence of -C=C-.

Running the *HP* 5890 GC/5970 Mass Spectrometer

You are already familiar with the general principles behind the operation of the gas chromatograph. The detector for the GC is a quadrupole mass spectrometer which has been described in the Background. Because each student is working with a different unknown, the analysis is not as automated as in a previous experiment. Be sure to follow the instructions carefully. The instructor will have turned on the instrument before class.

---

1. Press F2 to begin **Data Acquisition**.
2. Press F5 to **Load Parameters**. Type in place of the parameter file shown:
   PARAM:UNK1.A (substitute your unknown number for the 1)
3. Press F5 again to **Load** the actual parameter file. This is *very important*. If you simply press <Return>
   instead, the parameter file will <u>not</u> be loaded.
4. Press F1 to **Prepare to Inject**.
5. Press F4 if asked to **Overwrite Data File.**
6. Type in the data file space:
   DATA:UNK1.D (substitute your unknown number for the 1)
   Follow by <Return>. This is an insurance policy. If something happens and you need to retrieve your
   data again, it will be on the hard drive.
7. Use TAB to move to the operator name field and type in your name.
8. Wait for temperature equilibration and the message **Ready to Inject**.
9. Use the "empty syringe" method to inject your unknown and start the run. You may stop the run after the
   sample signal is recorded if there is still time remaining (F8).
10. Press F8 (**Exit**).
11. Press F8 (**Quit**).
12. Press F3 to enter the **Data Editor**.
13. Type *MSNORM ON* followed by <Return>. This "normalizes" all subsequent mass spectra generated to
    match a set of characteristics stored in the machine.
14. Press F1 to display the **Total Ion Chromatogram**.
15. Press F5 to display the set of **Spectrum** soft**Keys**.
16. Press F1 to generate a mass **Spectrum**.
17. Use the arrow keys (← →) to position the pointer at the top of the chromatogram peak. Press <Return>.
    The mass spectrum will be displayed above the chromatogram.
18. Hold down the **Shift** key and press **Print**.
19. Press F7 *twice* to get to a third set of spectrum keys.
20. Press F2 to tabulate the mass spectrum abundances. If there is more than one page, press F5 for each,
    sending them to the printer.
21. Press F8 *four times* to **Exit** and **Quit**.
22. Use the printer Line Feed to move your printouts to the nearest perforation and remove them.

You can obtain a copy of the **Beynon** program for your TI-83/84 calculator from the Link-equipped computers in the Resource Center. You will need to know the molar mass of your unknown and the % for the P+1 peak relative to the parent peak before running the program. You will be prompted to enter both and then the calculator will supply you with a list of formulas along with P+1 and P+2 data. You can copy these by hand or capture the screen on a Link-equipped computer and send the image to the printer.

Obtaining an NMR spectrum on the *Varian* **EM-360**

Note: All samples are 5% v/v solutions of the unknown in CDCl₃ which has been doped with TMS. Although the instructor will have tuned the spectrometer as precisely as possible before you run your sample, best results are obtained by touch-up tuning on each individual sample. This also corrects for gradual drift in the instrument. The tuning step is optional and is indicated below in *italic* type. You may skip it if you wish or if you do not feel confident in making the adjustments.

---

1. Check to see that all controls are set to their "boxed" or default positions if such are indicated. At this point do not change the position of any controls that do not have such positions marked. In particular, the Fine control on the Spectrum Amplitude controls (bottom left section of control panel) should be set to 10. The Sweep Zero control (lower second section from right on control panel) should be mid-range (5 turns from either end).

2. Select your sample from the rack and place it in the magnet console so that it will come to temperature while you do the preliminary set-up of the spectrometer.

3. Select the Methanol standard sample. Check the spinner height in the gauge on the front of the magnet console. Wipe the sample tube carefully with a kimwipe. Be sure the tube is clean. Any contaminants introduced into the spectrometer probe are likely to remain there for a very long time and result in impaired operation. Open the magnet probe access cover and place your finger over the air exhaust hole to temporarily increase air flow through the probe. Carefully insert the methanol sample tube into the probe. It should balance on the air flow if correctly inserted. Slowly withdraw your finger from the air exhaust hole so that the sample tube descends **gently** into the probe. It should begin to spin. If it does not, *ask for help*. Close the cover.

4. Place a sheet of scratch chart paper on the recorder table. By hand, gently move the pen carriage so that the pen is positioned at approximately δ 3.47 (the second red mark from the right). Press the **Parking Lock** on the recorder control panel. Use the Sweep Zero control to get a minimum pen deflection. You are now just off the main proton signal from the methyl group in methanol. This approximately zeros the sweep field. Press **Normal** on the recorder control panel. Open the magnet probe access cover and place your finger over the air exhaust hole. The sample tube should rise in the probe so that you can remove it. Place it in the rack inside the cover so that it will remain at temperature for the next student.

5. Carefully place a spinner on your sample tube and adjust it to the correct height using the gauge on the front of the magnet console. Wipe the sample tube carefully with a kimwipe and insert it into the probe as you did the Methanol sample. Close the lid.

6. Gently move the pen carriage by hand to the δ 0 mark (right-most red mark) and adjust the Sweep Zero control to achieve a maximum pen deflection. The field is now zeroed on the TMS signal but may drift a little before you are ready to record the spectrum. You can touch up this setting later.

7. Move the pen carriage by hand to the left, scanning for the greatest pen deflection. Once you have found it, move the carriage to the left of that signal. Press **Pen Up**, **Amplitude Set** and **Forward** on the recorder control panel. The carriage will move to the right and the pen will rise and remain at the highest deflection. When it stops rising, press **Stop**. Adjust the Spectrum Amplitude controls for maximum pen height on the chart without excess pen chatter or vibration. Press **Normal** and **Pen Auto** on the recorder control panel.

*8. Move the pen carriage by hand so that you are over the signal you just used to adjust the amplitude. Press **Resolution Adjust** on the recorder control panel. Note the position of the fine amplitude setting and adjust it as needed during the tuning process so that the pen remains at about 70% of maximum. Use the Resolution controls (lower right section of spectrometer control panel) to obtain maximum pen deflection. Adjust the **Y** control first and then the **Curvature**. Then repeat. These controls interact so retouching of one is necessary after adjusting the other. Major adjustments should not be needed. **DO NOT MAKE MAJOR ADJUSTMENTS IN THESE CONTROLS**. When you are satisfied with the adjustments, press **Normal** on the recorder control panel.*

9. Recheck that the spectrometer is still zeroed on the TMS signal. You may want to actually scan just that portion of the spectrum to be sure you have the signal adjusted closely to zero. The maximum pen deflection should correspond to the right-most red mark on the recorder platform. Use the Sweep Zero control to adjust if needed.

10. Remove the scratch paper (it can be used again) and place a sheet of chart paper on the recorder platform, making sure that the chart 0 is aligned with the right-most red mark. Gently move the pen carriage to the far left. Adjust the **Baseline** wheel so the pen is a little above the bottom chart axis. Press **Forward** on the recorder control panel. When the pen reaches the right side of the platform, press **Stop**. Congratulations! You now have an NMR spectrum of your unknown!

[Ah, but you still need to integrate.........]

11. Press **Pen Up** and **Auto Integrate** on the recorder control panel. Move the pen carriage by hand to the left of the left-most signal recorded (be sure the pen is over a place where there is <u>no</u> signal). Press **Reset** from the Integrator controls on the spectrometer control panel (upper left section). Alternately use **Reset** and **Balance** to eliminate pen drift. This is sometimes a very drawn out and annoying process. You can minimize frustration by not over-reacting to pen drift. Make only <u>small</u> changes in the **Balance** control, press **Reset**, and observe the result. Once balance is achieved, move the baseline up a little so the pen won't draw directly over the spectrum as it traces the integral. The baseline wheel is located on the recorder control panel.

If the spectrometer has been drifting a lot, you can retouch the sweep zero setting at this point by returning to Normal mode and moving the pen carriage to the TMS signal location. However, unless drift is very severe, you will get a usable--if shifted--integral spectrum without this adjustment. If you decide to make the adjustment, remember to return to Auto Integrate mode before continuing. You may also have to recheck the Balance.

12. Press **Forward** on the recorder control panel. Just before reaching the TMS peak (or chart 0), **Stop** the scan. Press **Hold** on the Integrator controls (a red light should come on). Now adjust the Fine amplitude control (and Coarse, if needed) for maximum pen travel without "topping out". Move the carriage by hand to the left of the left-most signal, press **Hold** again (to release--red light goes out) and then **Reset**. Press **Pen Auto** on the recorder control panel and then **Forward**. **Stop** the scan when the carriage has reached its farthest travel or just before the TMS peak. Return the recorder to **Normal** and remove your chart paper. **DO <u>NOT</u> SHUT OFF THE INSTRUMENT!!!!!!!!!!!!!!** Carefully eject your sample from the magnet console and remove the spinner. Place your unknown in the rack with the other samples. Close the magnet probe access cover.

Recording the IR spectrum on the *Perkin-Elmer* **1420**

Unlike the previous two instruments, infra-red spectrometer is fairly simple to operate. Most settings can be left in their default positions. Your sample is dropped onto a small disc of AgCl. This disk has a very thin ridge on one side but is flat on the other. When two discs are placed with their ridges together they form a small compartment that is 0.50 mm thick. When one disc is turned so that its flat side meets the ridge of the other a compartment 0.25 mm thick results. For pure liquids both of these sample thicknesses are often too great so we will run all samples as *thin films*, i.e., with the flat sides of the discs facing each other. Prepare your sample in the fume hood. **NO SAMPLES SHOULD BE PREPARED ON THE WOODEN TABLE SUPPORTING THE SPECTROMETER**.

Place one disc in the holder so its flat side faces up. Handle the discs by the edges. They are fragile. Place two drops of your unknown on the disc and put a second disc (flat side facing down) on top of it. Screw together the sample holder and place it in the sample bracket in the *front* of the sample compartment of the spectrometer (the sample holder *nearest* to you).

1. Press **1** for the Chart Expansion.
2. Press **3** for the Scan time/slit width.
3. If the chart paper is not aligned with the pen at 4000 cm^{-1} press **Chart** and then use the Parameter Adjust buttons (↑↓) to move the paper 1 cm at a time. Then press **Chart** again.
4. Press **Baseline** and use the Parameter Adjust buttons (↑↓) to move to pen to about 60% transmittance. Press **Baseline** again when finished.
5. Press **Scan**. A medium resolution scan will be completed in about 3 minutes.
6. Use scissors to cut off the chart paper at the conclusion of the scan.
7. Remove the sample from the sample compartment and take it to the fume hood. Unscrew the holder and remove the discs. Separate them and wash with two or three drops of acetone. Dry with Kimwipes and place in the dark again.

The physical tests consist of any two of boiling point, density and refractive index determination. Boiling point and density determination will not be discussed here. The student should be able to conduct these without any assistance based on earlier work. Remember, the unknown is given in finite quantity. Liquid from these two tests can and should be returned to the sample vial.

Refractive index or the *index of refraction* of a substance is a characteristic property. It is the ratio between the speed of light in a vacuum (*c*) and the speed of light in the substance (v):

$$n = \frac{c}{v}$$

The refractive index of most liquids is in the range of 1.3 to 1.8. It is 1.3 to 2.5 or higher for solids. Three significant variables affect the value obtained for refractive index. They are temperature, wavelength of radiation, and pressure.

The temperature effect is largely one of changing density. For many liquids, the temperature coefficient of refractive index lies in the range of -4 to -6 x 10^{-4} per ^{o}C. The temperature factor, although small, should be kept in mind when comparing measured values of *n* to handbook values. The temperature at which the handbook value was measured is generally given as a superscript to *n*.

The refractive index of a transparent medium generally decreases with increasing wavelength. The D line from a sodium vapor lamp (λ = 5.893 x 10^{-7} m) is most commonly used as a source for recording refractive indices and the data obtained is designated as n_D. The simple instrument you will be using is compensated to give similar values using ordinary white light.

The refractive index of a substance increases with pressure because of the accompanying rise in density. The effect is most pronounced with gases and is of little consequence in other than exacting work with liquids and solids.

The instructor will demonstrate the operation of the refractometer.

The Report

When you have gone through all of your data, a summary is in order. You should move through the *entire* process briefly. Just to be sure, you should address all of the following:

- Qualitative tests
- Molecular formula (MSpec)
- Proton ratio (NMR)
- Chemical shift analysis (NMR) [you must identify each relevant shift with a structural element]
- Probable structure
- Fragment analysis (MSpec) [a few major fragments will suffice]
- Confirmation analysis (IR) [functional groups or some other structural component]
- Physical data comparison

Qual tests should be used to indicate why you chose one type of compound over another. If you used correlation charts from sources other than your lab text (there are some in the CRC and others online), you should indicate the sources. For the physical tests, you should certainly give *literature references* to back up your claims. The goal here is to give a logical flow to your identification similar to--but not as detailed as--what is given in the Background section for the examples. A 3D molecular structure for your unknown(s) is(/are) also required.

Table of Common Fragments

Note: this table is not exhaustive but instead represents fragments you are likely to encounter in the simpler kinds of compounds we study in this course. In this table, as in all of the tables in this section, the benzene ring is represented by ϕ.

Common Fragment Ions

m/e	ions
15	CH_3
17	OH
26	$C\equiv N$
29	C_2H_5, $CH(=O)$
31	CH_2OH, OCH_3
43	C_3H_7, $CH_3C(=O)$, C_2H_5N
45	CH_3CHOH, CH_2CH_2OH, CH_2OCH_3, $C(=O)OH$
57	C_4H_9, $C_2H_5C(=O)$
59	$(CH_3)_2COH$, $CH_2OC_2H_5$, $C(=O)OCH_3$, CH_3OCHCH_3, CH_3CHCH_2OH
71	C_5H_{11}, $C_3H_7C(=O)$
77	C_6H_5
87	$C_3H_7C(=O)O$, $CH_2CH_2C(=O)OCH_3$
91	ϕ-CH_2
101	$C(=O)OC_4H_9$
105	ϕ-$C(=O)$, ϕ-CH_2CH_2, ϕ-$CHCH_3$
107	ϕ-CH_2O, CH_2-ϕ-OH
119	ϕ-$C(CH_3)_2$, CH_3-ϕ-$CHCH_3$, CH_3-ϕ-$C(=O)$
121	OH-ϕ-$C(=O)$, CH_2-ϕ-OCH_3

Table of Common Fragments Lost

Sometimes fragment peaks are more easily interpreted if considered as "fragments lost" rather than specific fragment ions (for example, P-17 in an alcohol represents loss of -OH). The table below gives some of these values and their usual assignments. **Most species are radicals.**

Common Fragments Lost

Parent minus	Fragment lost
1	H ·
15	· CH$_3$
17	· OH
26	CH≡CH, · C≡N
28	CH$_2$=CH$_2$
29	CH$_3$CH$_2$ ·, · CH(=O)
31	· OCH$_3$, · CH$_2$OH, CH$_3$NH$_2$
43	· C$_3$H$_7$, · C(=O)CH$_3$
59	· C(=O)OCH$_3$, CH$_3$C(=O)NH$_2$
73	· C(=O)OCH$_2$CH$_3$

Tables of Common Chemical Shifts

The first table in this section gives values for the chemical shifts of protons on a **β-carbon** attached to a functional group, i.e., the protons in question are attached to a carbon which is attached through an additional carbon to a functional group. Consider the example below:

$$H_3C\text{-}CH_2\text{-}OH$$

β carbon ⟶ ⟵ α carbon
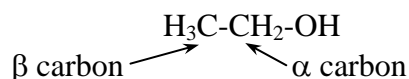
In this example, the β-carbon is a *methyl* group ($-CH_3$) but it could also be a *methylene* group ($-CH_2-$) or a *methine* group ($-CH-$). Protons in these slightly different structural environments will have slightly different shifts. An attempt has been made to show this in the table that follows. In each structural environment represented the **M** stands for the β-carbon (actually, its attached hydrogens). So the sample structure above corresponds to the entry in the second row of the table, **M**-C-OH. The appropriate chemical shift (since this is a methyl group) would be about $\delta = 1.2$.

As with the **Table of Common Fragments**, these tables are not meant to be exhaustive resources.

M-C-NO₂	CH				CH₂			CH₃																		
M-C-OH						CH		CH₂			CH₃															
M-C-OR						CH		CH₂			CH₃															
M-C-Oφ					CH					CH₂			CH₃													
M-C-OC(=O)R								CH	CH₂			CH₃														
M-C-OC(=O)φ									CH	CH₂	CH₃															
M-C-CH₂										CH			CH₂			CH₃										
M-C-C=CR₂										CH		CH₂			CH₃											
M-C-C≡CR								CH			CH₂			CH₃												
M-C≡N						CH			CH₂				CH₃													
M-C-φ							CH			CH₂				CH₃												
M-C-C(=O)R							CH			CH₂					CH₃											
M-C-C(=O)OR							CH		CH₂					CH₃												
M-C-C(=O)φ							CH			CH₂				CH₃												
M-C-C(=O)H									CH₂						CH₃											
$\delta \longrightarrow$	0.5	0.4	0.3	0.2	0.1	**2**	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	**1**	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	**0**

The table that follows gives similar information for hydrogens on **α-carbons**.

M-NO₂			CH	CH₂	CH₃																
M-OH							CH	CH₂	CH₃												
M-OR							CH	CH₂	CH₃												
M-Oφ			CH				CH₂	CH₃													
M-OC(=O)R	CH						CH₂		CH₃												
M-OC(=O)φ	CH					CH₂		CH₃													
M-C=C																	CH₂		CH₃		
M-C≡C												CH		CH₂		CH₃					
M-C≡N												CH		CH₂	CH₃						
M-φ												CH	CH₂		CH₃						
M-C(=O)H														CH₂	CH₃						
M-C(=O)R												CH	CH₂		CH₃						
M-C(=O)φ											CH		CH₂	CH₃							
M-C(=O)OR													CH	CH₂	CH₃						
$\delta \longrightarrow$	**5**	0.8	0.6	0.4	0.2	**4**	0.8	0.6	0.4	0.2	**3**	0.8	0.6	0.4	0.2	**2**	0.8	0.6	0.4	0.2	**1**

Protons on *alkene* carbons generally appear as clustered peaks similar to the splitting of signals observed for the protons on a substituted benzene ring. It is often possible to distinguish individual proton signals. Common shifts are given in the table below.

structure	0.4	0.2	7	0.8	0.6	0.4	0.2	6	0.8	0.6	0.4	0.2	5	0.8	0.6	0.4	0.2	4	0.8
Ha,Hb>C=C<Hc,R										Hc	HbHa								
Ha,R>C=C<Hb,R									Ha	Hb									
Ha,Hb>C=C<Hc,OC(=O)R		Hc											Hb		Ha				
Ha,Hb>C=C<Hc,φ			Hc										Hb		Ha				
H₃C,Ha>C=C<Hb,φ ($H_3C,Ha>C=C<Hb,\phi$)							Hb	Ha											
Ha,Hb>C=C<CH₃,C≡N							Hb	Ha											
H₃C,Hb>C=C<Ha,CH(=O)				Hb		Ha													
H₃C,Hb>C=C<Ha,C(=O)OH			Hb					Ha											
Ha,Hb>C=C<CH₃,C(=O)OH						Hb		Ha											
R,Hb>C=C<Ha,CH(=O)	Hb			Ha															
Ha,Hb>C=C<Hc,OR					Hc													Hb	Ha
δ ⟶	0.4	0.2	7	0.8	0.6	0.4	0.2	6	0.8	0.6	0.4	0.2	5	0.8	0.6	0.4	0.2	4	0.8

Protons on *benzene rings* typically absorb in the range of δ = 6-8. Shifting takes place because of the substitution of functional groups. Asymmetric poly-substitution gives rise to a number of splitting patterns which range from simple to very complex and shift values depend not only on the position on the ring relative to another group but also on the identities of the groups themselves. Thus the values given in the table below should be treated as good estimates. Recall that the older designations *ortho* (o), *meta* (m) and *para* (p) refer to 1,2 or 1,3 or 1,4 di-substitution.

	0.4	0.2	8	0.8	0.6	0.4	0.2	7	0.8	0.6	0.4
Benzene							•				
NH₂ m,p,o								•		•	•
NO₂ o,p,m		•		•	•						
OH (m,p,o)								•		•	•
OR m,(op)								•		•	
CH₃								•			
C=CH₂						•					
C≡CH o,(mp)							•	•			
C≡N							•				
CH(=O) o,p,m				•	•	•					
C(=O)CH₃ o,(mp)				•		•					
C(=O)OH o,p,m				•	•	•					
C(=O)OR o,p,m		•			•	•					
δ →	0.4	0.2	8	0.8	0.6	0.4	0.2	7	0.8	0.6	0.4

Aldehyde protons are generally shifted far to the left relative to TMS. In aliphatic aldehydes [RCH(=O)] the typical shift is $\delta = 9.7$. For aromatic aldehydes [ϕCH(=O)] $\delta \approx 10$. **Formyl** protons are also typically shifted to the far left. In structures like **H**C(=O)OR the shift is around $\delta = 8.05$.

Protons subject to *hydrogen bonding* occur in a number of different structures. The most common are those in alcohols, amines, and carboxylic acids. The degree to which hydrogen bonding occurs has a dramatic effect on the chemical shift even for similar types of compounds and so *ranges* rather than specific values for the chemical shifts are given below.

Proton	Class															
O**H**	carboxylic acids		————————													
	alcohols											————————				
NH$_2$ and NHR	aliphatic amines												———————			
	aromatic amines									———						
	$\delta \longrightarrow$	14	13	12	11	10	9	8	7	6	5	4	3	2	1	0

Finally, methylene groups (-CH$_2$-) attached to two functional groups, i.e., X-CH$_2$-Y, have specific shift values associated with the combination of functional groups. Some of the more common combinations are given in the table that follows.

Groups	-C(=O)ϕ	-OH	-OR	-Oϕ	-OC(=O)R	-CH$_3$	-C=C	-ϕ	-C(=O)R	-C(=O)OR
-C(=O)OR	3.62	4.34	4.13	5.09	4.91	2.25	3.00	3.40	3.37	3.35
-C(=O)R	3.77	4.49	4.29	5.16	4.42	2.47	3.25	3.55	3.60	
-ϕ	3.92	4.58	4.70	4.90	5.08	2.55	3.30	3.97		
-C=C	3.39	4.13	3.95	4.78	4.68	2.02	2.60			
-CH$_3$	2.54	3.70	3.40	3.93	4.25	1.17				
-OC(=O)R	5.20	5.92	5.72	6.59	6.46					
-Oϕ	5.30	6.02	5.82	6.69						
-OR	4.43	5.15	4.55							
-OH	4.63	4.55								
-C(=O)ϕ	3.91									

Table of IR Vibrational Bands

The correlation charts for *IR vibrational bands* which follow use a shorthand to represent different intensities of absorptions: S = strong, M = medium, W = weak. "v" used before one of these indicates that the absorption is variable and may be missing. Sharp absorptions are indicated with the letter only while broader signals are enclosed by short line segments which roughly cover the range. Remember that the overall structure of a particular molecule can move specific vibrational frequencies somewhat, so like the NMR shifts, these absorptions should be read as good estimates.

wavenumbers, cm^{-1} →		2	3	4	5	6	7	8	9	10	11	12	13	14	15
		5000	3000	2500	2000	1800	1600	1400	1200	1000	900	800		700	
alkanes			M				M	M			—W—			W	
alkenes															
	CH$_2$=CHR		MM			M	M	M		S	S				
	trans		M				vW			S					
	cis		M				M							—S—	
	CR$_2$=CH$_2$		M		M		M				S				
	CR$_2$=CHR		W				W					—M—			
	CR$_2$=CR$_2$						vW								
alkynes															
	monosub		S		W			—W—							
	disub				W										
benzenes															
	monosub		W			—W—	MW	MM		M	M		—S—	—S—	
	1,2 disub		W			—W—	MW	MM	M	M			—S—		
	1,3-disub		W			—W—	MW	MM	—M—		—M—	—S—		—S—	
	1,4-disub		W			—W—	MW	MM	M	M	—S—				
	1,2,4-trisub		W			—W—	MW	MM			—M—	S			
	1,2,3-trisub		W			—W—	M	M					S	—M—	
	1,3,5-trisub		W			—W—	M	M			—S—			—M—	
alcohols															
	free OH		S												
	weak H-bond (intra)		M												
	strong H-bond (intra)		—M—												
	inter. H-bond		—S—												
	sat. 3° or sym. 2°								—S—						
	sat. 2°								—S—						
ethers															
	aliphatic								—S—						
	aromatic (ϕ-O-CH$_2$)							—S—		—M—					
carbonyls															
--ketones															
	dialkyl [-CH$_2$C(=O)CH$_2$-]					S			—M—						
	aromatic					S		—M—							
--aldehydes															
	aliphatic			M		S	M								
	aromatic			M		S	M								
--carboxylic acids															
	dimer		—S	MM		S	M	—S—			—M—				
	carboxylate ion					S	M								
--esters															
	formates					S		—S							
	acetates					S		S		M (acetate of primary alcohol)					
	other aliphatic					S		—S							
	aromatic					S		S—	M						
amines															
--primary															
	aliphatic		MM				M			—M—		—S—			
	aromatic		MM				M	S					—M—		
--secondary															
	aliphatic		W												
	aromatic		W							—M—			—M—		
--tertiary															
	aliphatic									—M—					
	aromatic								—S—						
nitriles															
	aliphatic				W										
	aromatic				W										
nitro compounds															
	aliphatic					S	M								
	aromatic					S	—M—					—S—			
wavelength, μ →		2	3	4	5	6	7	8	9	10	11	12	13	14	15

In addition to the absorptions on the previous page it is often possible, particularly with slow scans, to pick out details related to the structural environment of methyl and methylene groups. A few of the more common vibrations are given below.

CH$_3$ Group Absorptions

CH$_3$-C(=O)-	(ketone)	1450-1400 and 1375-1350 cm^{-1}
		(6.90-7.15 and 7.28-7.41 μ)
CH$_3$-O-R		2832-2815 and 1470-1440 cm^{-1}
		(3.53-3.55 and 6.80-6.95 μ)
CH$_3$-C(=O)O-		14500-1400 and 1400-1340 cm^{-1}
		(6.90-7.15 and 7.15-7.46 μ)
CH$_3$-NR$_2$		2820-2760 and 1440-1390 cm^{-1}
		(3.55-3.62 and 6.95-7.20 μ)

CH$_2$ Group Absorptions

-CH$_2$-C(=O)-	(aliphatic)	1435-1405 cm^{-1}
		(6.97-7.11 μ)
	(aromatic)	1475-1425 cm^{-1} (multiple bands)
		(6.78-7.02 μ)
-CH$_2$-O-	(aliphatic)	1470-1435 cm^{-1}
		(6.80-6.97 μ)
	(aromatic)	1500-1470 cm^{-1} (multiple bands)
		(6.67-6.80 μ)
-CH$_2$-O-C(=O)-		1475-1460 cm^{-1}
		(6.78-6.85 μ)
-CH$_2$-NR$_2$		2820-2760 and 1475-1445 cm^{-1}
		(3.55-3.62 and 6.78-6.92 μ)
-CH$_2$-C≡N		1425 cm^{-1}
		(7.02 μ)

Adapted from <u>Principles of Instrumental Analysis</u>, Douglas A. Skoog, Donald M. West

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<u>Organic Chemistry On-Line</u>, http://homework.chem.uic.edu/, Paul R. Young